In presenting the dissertation as a partial fulfillment of the requirements for an advanced degree from the Georgia Institute of Technology, I agree that the Library of the Institute shall make it available for inspection and circulation in accordance with its regulations governing materials of this type. I agree that permission to copy from, or to publish from, this dissertation may be granted by the professor under whose direction it was written, or where such copying or publication is solely for scholarly purposes and does not involve potential financial gain. It is understood that any copying from, or publication of, this dissertation which involves potential financial gain will not be allowed without written permission.

_____

_____

THE HIGH TEMPERATURE REACTIONS OF CARBON MONOXIDE WITH IRON, NICKEL, AND AUSTENITIC STAINLESS STEEL

A THESIS

Presented to

The Faculty of the Graduate Division

by

Arthur Reeves Cox

In Partial Fulfillment

of the Requirements for the Degree

Master of Science in Metallurgy

Georgia Institute of Technology

December, 1962

5 a
12R

THE HIGH TEMPERATURE REACTIONS OF CARBON MONOXIDE WITH IRON, NICKEL, AND AUSTENITIC STAINLESS STEEL

Approved:

Date approved by Chairman: 12-5-62

ACKNOWLEDGMENTS

The author wishes to express his appreciation to his thesis advisor, Dr. R. F. Hochman, who suggested this research project and contributed invaluable aid during the entire course of work.

Sincere thanks are extended to Dr. N. N. Engel, who helped considerably in developing experimental techniques and in evaluation of results; to Dr. E. J. Scheibner, who made possible the use of otherwise unavailable equipment; and to Dr. H. V. Grubb, who made available funds to support the program.

To Mr. J. W. Johnson and Mr. W. P. Edmondson, of the Georgia Tech Engineering Experiment Station, gratitude is given for their fine efforts in electron microscopy and specimen preparation, respectively.

The author also wishes to thank Mr. J. D. Goodrich and those members of the School of Chemical Engineering who gave freely of their time and energy.

Numerous people who have contributed to this program have not been individually acknowledged. It is hoped that they will realize appreciation is due them.

To my fiancée, Miss Patricia Rhoads, my devoted thanks for typing the entire manuscript.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

SUMMARY

The high temperature reactions of carbon monoxide with iron, nickel, and AISI Type 316 stainless steel were studied. The purposes of this research were to determine the products formed by interaction of metal with carbon monoxide, and to investigate the mechanism of reaction with Type 316 stainless steel.

The experimental work was done at 1200°F. and at essentially atmospheric pressure. Electron transmission specimens of pure iron, pure nickel, and Type 316 stainless steel were exposed for periods from 1 to 45 minutes in order to determine the reaction products. Evaluations were made entirely by electron microscopy and selected area diffraction. Wire samples of Type 316 stainless steel were exposed for periods ranging from 1 to 72 hours in order to investigate the kinetics of reaction. Analytical work using these specimens was done which employed weight changes, electrical resistance changes, x-ray diffraction, infrared absorption, and metallurgical techniques.

The results in general showed that the carbon monoxide reaction with iron resulted in the formation of an iron

carbide, suggested to be $Fe_{20}C_9$, with a simultaneous or subsequent formation of elementary carbon. Nickel was found to be unreactive at this temperature. Nickel oxide was reduced to pure metal with no observable deposition of elementary carbon.

The reaction with Type 316 stainless steel proceeded through the formation of an unidentified carbide, suggested to be a form of iron carbide, with a simultaneous or subsequent formation of elementary carbon. Kinetic data and further examinations strongly suggested that the reaction involving Type 316 stainless steel was autocatalytic, dependent on the formation of an unstable carbide and on diffusion of carbon into the metal. Conclusive evidence of the mechanism was not obtained.

CHAPTER I

INTRODUCTION

In the presence of a suitable catalyst and at temperatures about 1000°F., carbon monoxide decomposes according to the reaction

$$2CO_{(g)} = CO_{2(g)} + C_{(s)}.$$

Associated with this decomposition is a reaction of carbon monoxide and/or its decomposition products with the catalyst. This reaction has been observed to deleteriously affect the catalyst.

Iron, nickel, cobalt, and their oxides have been observed to actively promote, or catalyze, the decomposition of carbon monoxide. Numerous alloys containing these elements also show a catalyzing behavior. Most austenitic stainless steels (300 series, iron-chromium-nickel alloys), normally suitable for use at elevated temperatures, are among the alloys which promote this decomposition. These materials are

affected to the extent that they suffer a decrease in mechanical strength and embrittlement, which result in their ultimate failure.

Because of the adverse effect accompanying the decomposition of carbon monoxide on these catalyzing agents, investigations had been undertaken to determine the type of attack and to explain the mechanism or mechanisms by which it proceeds. These studies, as well as industrial experiences, have categorized the attack as an unusual form of elevated temperature corrosion. Carbon resulting from the decomposition deposits primarily as graphite. Beneath regions of deposition, the surface of the catalyst is attacked and further carbonaceous precipitate occurs in the grain boundaries. The overall result is a metal removal from the solid matrix into the surface deposits.

Several theories on the mechanism of this metal removal have been published. They are independent of each other and involve much controversy. They are:

1. Formation of an unstable gas phase intermediate reaction product, such as a metal carbonyl, which subsequently decomposes to free metal and carbon monoxide.

2. Formation of a solid phase intermediate reaction product, such as a metal carbide, which subsequently

decomposes to free metal and carbon.

3. Metal wastage due to mechanical forces generated by the decomposition in grain boundaries causing fracture or removal of individual grains.

The present work was undertaken because of the restricting effect this attack places upon the use of most 300 series austenitic stainless steels. The purpose of this research was to investigate the high temperature reaction occurring during the decomposition of carbon monoxide with austenitic stainless steel, and to investigate further the reactions occurring with its catalytic alloying elements, iron and nickel. This was to be accomplished by reacting samples of iron, nickel, and austenitic stainless steel in a chemically pure carbon monoxide atmosphere at 1200°F. Several methods, including electron microscopy and x-ray diffraction, were to be used to identify the reaction products and observe the changes in the metal. The final objective of this study was to formulate, if possible, a basis for the attack of the catalyst during the decomposition of carbon monoxide and to relate this to the theories already presented with the hope that an improved concept of the reaction could be obtained.

CHAPTER II

A SURVEY OF PREVIOUS WORKS

Numerous investigations of the high temperature reactions and attack of iron, nickel, and 300 series stainless steels by carbon monoxide have been published. The results in all cases showed that carbon monoxide was detrimental to the stability and usefulness of these metals. While many investigations were concerned with identification of reaction products, a large effort had been directed toward the determination of temperature and pressure dependence, gas compositions, and other external conditions for which the reaction would proceed. The ultimate goal of most of these works was to ultilize the results to predict a mechanism by which the solid was engaged. The following is a compilation of the important researches done in this field which have a direct bearing on this project.

Work of W. Baukloh (1)

In 1940, Baukloh published his work describing the destructive action of gases composed in part of carbon

monoxide and carbon dioxide. He states:

> The destructive effects of carbon monoxide and CO-containing gases find their hypothesis mainly in the possibility of the carbon monoxide reacting according to equation (1) $2CO = C + CO_2$. They always appear when the reaction proceeds from left to right, i.e., with the formation of solid carbon. Up to relatively high temperatures, ca. 1000° [F.], pure carbon monoxide tends to undergo partial decomposition with separation of solid carbon.

The equilibrium diagram for carbon monoxide-carbon dioxide is reproduced in Figure 1. Field 1 in the figure is the region in which carbon monoxide will decompose. Baukloh infers that only in this region will attack of metals occur, since destruction is dependent on the formation of free carbon.

In a series of experiments with cast iron, he noticed a crumbling effect of the solid when large depositions of carbon were achieved. Working similarly with engineering alloys, he detected no destructive effect. He continued his work using metallic oxides and other metals as catalysts. Also, he investigated further the relationship between attack and carbon monoxide-carbon dioxide compositions.

Concluding his work, Baukloh theorized that the destructive effect of carbon monoxide-containing gases was due to deposition of carbon in porous regions of the material (cast iron, iron oxide, etc.) and that these depositions created

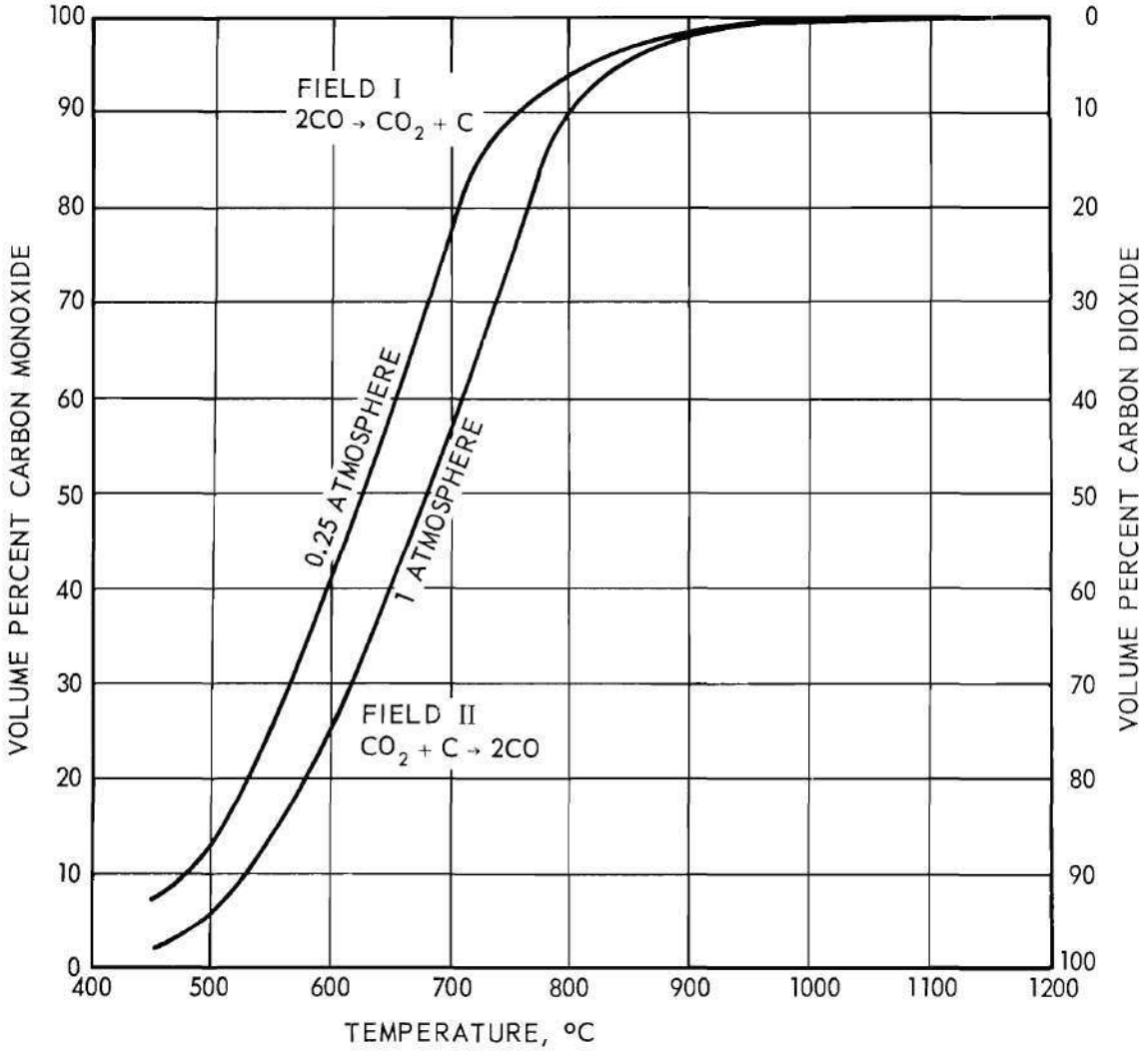


Figure 1. Equilibrium Diagram for the Reaction 2 CO $\rightleftharpoons$ C + CO_2.

large enough pressures to cause mechanical failure or fracture. Further, dense materials were not affected because the carbon monoxide could diffuse into the metal only in monomolecular form with no resulting decomposition. His observations also indicated that typical carbide formers, iron, nickel, cobalt, and oxides which could be reduced to the metallic state in Field 1, were suitable catalysts for the dissociation.

Work of A. Juliard, R. Rayet, and A. Ludé (2)

In 1948, Juliard, Rayet, and Ludé completed a study of the dissociation of carbon monoxide in the presence of metallic oxides. Their objectives were to obtain the rate of reduction of iron oxide and nickel oxide according to the reaction

$$MeO + CO = Me + CO_2$$

where Me = metal

and the rate of dissociation of carbon monoxide in the temperature range of 600°C. to 800°C.

Their results indicated that the rate of reduction of nickel oxide (NiO) varied in the same manner as observed for reductions in which no elementary carbon from decomposition

of carbon monoxide occurred. Decomposition began at the same time as the reduction did, and the rate increased linearly during the reduction. When the oxide was almost all converted, the decomposition rate increased but became linear again once the reduction was completed. Using nickel obtained in this manner in a repeated experiment, no dissociation of carbon monoxide took place. Nickel oxide reduced by hydrogen to pure metal was substituted for the nickel reduced by carbon monoxide and dissociation again occurred.

Iron oxide was reduced in a carbon monoxide atmosphere according to

$$Fe_2O_3 \text{ to } Fe_3O_4 \text{ to } FeO \text{ to } Fe.$$

Dissociation did not begin until free iron (the metallic state capable of being carburized) appeared in the specimen. It then proceeded similarly to that with nickel.

The evidence collected from this study has much importance. Pure nickel obtained from reduction by carbon monoxide was not observed to catalyze the decomposition reaction but nickel obtained from reduction by hydrogen did. The authors felt that a possible explanation of this phenomena could be

that hydrogen absorbed on the nickel crystallites reduced the carbon monoxide.

With regard to iron and its oxides, it was concluded that dissociation could not occur until the oxides had been reduced sufficiently to allow the formation of free iron. The authors believed their work was evidence that decomposition of carbon monoxide could not start in contact with pure metal, but rather, required the presence of an interface like Ni-NiO or Fe-Fe_3C, or the prior formation of carbon nuclei.

Work of W. R. Davis, R. J. Slawson, and G. R. Rigby (3)

In 1953, the authors completed an investigation of the carbon deposits in the brickwork of blast furnaces. Using electron microscopy, it was observed that the carbon was in the form of minute vermicular growths. The carbon in this form occurred at about 450°C. by the interaction of carbon monoxide and iron oxide at iron spots in the brick refractories. X-ray analysis of the deposits showed them to be composed of amorphous carbon, cementite (Fe_3C), and an iron percarbide ($Fe_{20}C_9$). It was suggested that the following reactions may have taken place:

$$Fe_3O_4 + CO = 3FeO + CO_2$$

$$FeO + CO = Fe + CO_2$$

$$3Fe + 2CO = Fe_3C + CO_2.$$

It was further suggested that the cementite could continue to react accordingly:

$$Fe_3C = 3Fe + C$$

$$20Fe_3C + 14CO = 3Fe_{20}C_9 + 7CO_2$$

$$3Fe_{20}C_9 = 20Fe_3C + 7C.$$

Under these reaction possibilities, the authors postulated that the catalyst for the dissociation could be iron, alternately converted to cementite and back to iron, or cementite, alternately converted to percarbide and back to cementite.

Work of W. B. Hoyt and R. H. Caughey (4)

In 1959, Hoyt and Caughey concluded a study of the effect of carbon monoxide-containing gases on stainless steel. Industrial experience had shown that synthesis gas containing 12 to 20 per cent carbon monoxide attacked Type 310 stainless steel in the temperature range of 1200°F. to 1300°F. In an extensive metallurgical examination of the affected metal, they were able to describe thoroughly the

corrosive aspects of the reaction.

Immediate observations showed severe pitting on the surface which had been in contact with the gases. Microscopic examination showed in every case that the pitting and metal loss associated with it were due primarily to carburization. Additional chemical analyses, x-ray diffraction, ignition spectrographic procedures and mechanical tests indicated the following:

1. Carbon diffusion from the heavily carburized surface of the specimen took place predominantly along intergranular paths.

2. Only intergranular carbide precipitation was noticeable in areas removed from the surface.

3. X-ray diffraction indicated the presence of iron oxides on the surface.

4. Affected areas were brittle and hard.

In a discussion of possible theories, the authors considered the following worthy of careful consideration. Under certain temperature and pressure conditions, iron and nickel catalytically promote the reaction $2CO = CO_2 + C$. The carbon resulting from the reaction is chemically active and can readily combine to form a carbide on the metal

surface. The carbide thus formed can be lifted from the surface by carbon depositions and carried into the gas stream.

Work of Ya. B. Kagan, A. N. Bashkirov, E. V. Kamzolkina, and A. Ya. Rozovsky (5)

Also in 1959, the authors explored the kinetics of conversion of carbon monoxide in the presence of iron catalysts. The experiments undertaken were maintained at atmospheric pressure in the temperature range of 270°C. to 410°C. Carbon monoxide was passed over iron with enough speed to assure considerable excess. The catalysts were prepared by reducing iron oxides in hydrogen at 800°C.

In their initial investigations, decomposition of carbon monoxide occurred only with the simultaneous formation of iron carbide according to the reaction

$$2Fe + 2CO = Fe_2C + CO_2.$$

In the temperature interval 240°C. to 370°C. the activity of the applied iron catalyst increased gradually until a maximum activity was reached and then remained constant. Above 370°C., a second maximum activity was reached.

Their investigations suggested that the initial contact of carbon monoxide with iron resulted in the formation of Hagg carbide, Fe_2C. The carbide reaction had an autocatalytic effect, which, as pointed out, is usual in the majority of reactions involving solids. The initial increase of catalytic activity was therefore predicted due to the appearance and growth of the new carbide phase. At temperatures below 370°C., deposition of elementary carbon begins only after the maximum speed of carbide formation is reached. The rate of deposition increases to a maximum, then gradually decreases. Above 370°C., i.e., at 410°C., a second higher maximum rate of deposition is reached. Dissociation occurs similarly to that observed at the lower temperature except the rate is greater. This was interpreted to be due to the growth of the carbide phase with an additional catalytic effect from the elementary carbon.

Work of W. B. Seagraves (6)

In 1960, Seagraves completed a study of the corrosive effects of high purity carbon monoxide on AISI Type 304 stainless steel, commercially pure nickel, and Inconel. His experimentation was done in the temperature range of 920°F. to 1100°F. and at atmospheric pressure. Exposure times

ranged from 4 to 120 hours Analytical work employed chemical, x-ray diffraction, x-ray flourescence, electron microprobe, microscopic and metallurgical techniques.

Experimental results on pure nickel and Inconel were limited. In all cases, an increase in weight from carbonaceous reaction products was obtained. The temperature dependency of the weight increase was not determined for these materials.

Experiments involving Type 304 stainless steel showed a definite temperature dependency in the range of 900°F. to 1100°F. Figure 2 is a reproduction of Seagraves' data showing the per cent weight increase due to carbonaceous deposits as a function of temperature for exposure periods of sixteen hours. Analyses of the surface deposits collected from exposed stainless steel were inconclusive. The presence of graphite, alpha-iron and an iron-nickel alloy was suggested. Microscopic examination showed a number of metallic-like particles enmeshed in the deposits.

Observations of the cross-sectional areas of exposed wires revealed penetration of attack along intergranular paths. In several examinations, it appeared the reaction in the grain boundaries generated mechanical pressures sufficient to cause fracture of individual grains with subsequent deposit

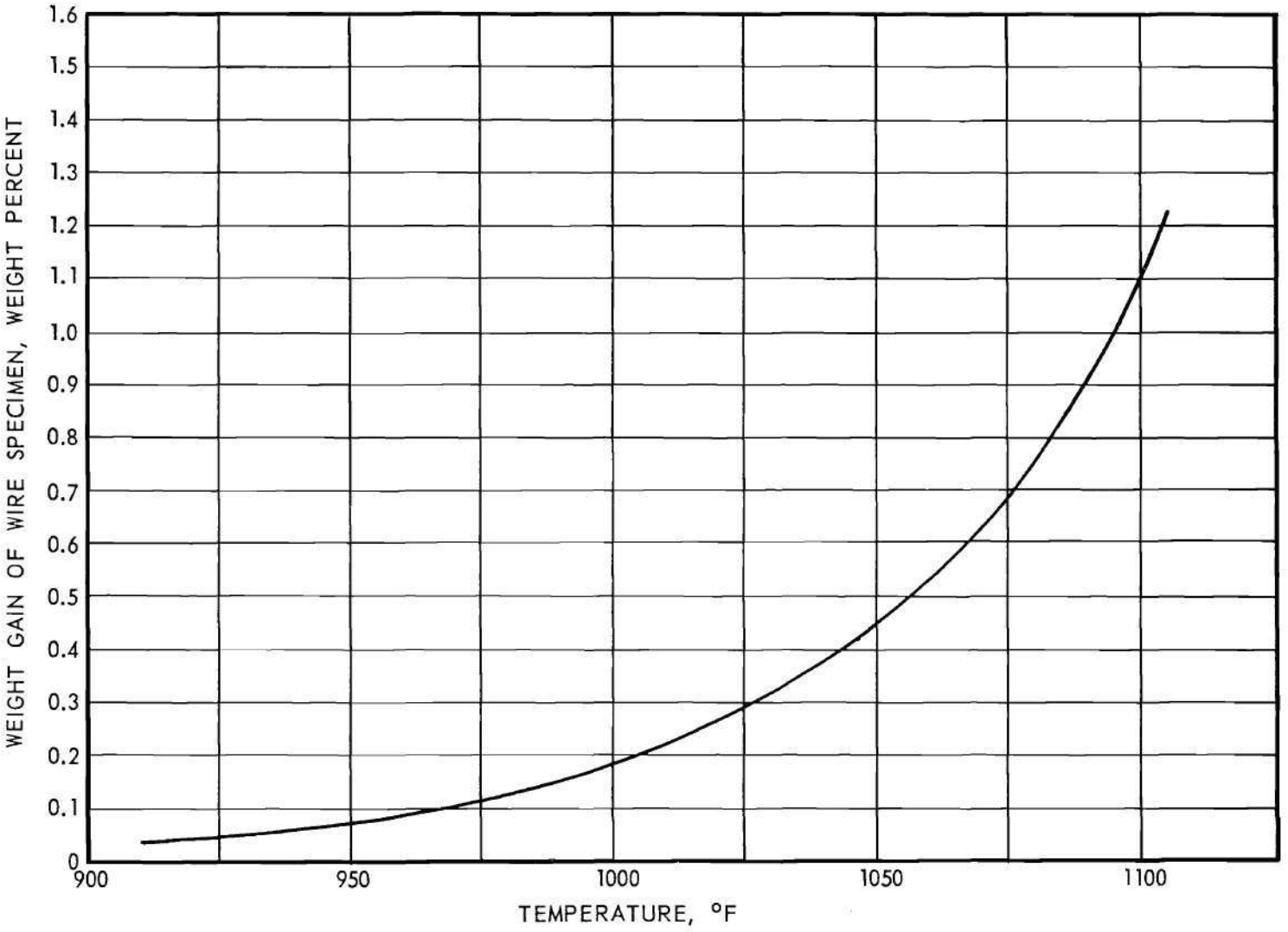


Figure 2. Weight Gain of Type 304 Stainless Steel Wire Specimen Exposed to Carbon Monoxide versus Temperature.

in the carbonaceous regions. Electron microprobe analyses of grains partially removed from the matrix because of intergranular deposition showed the composition was comparable to the original composition of the specimen, except near the surfaces, where a large depletion of iron had occurred.

From his works, Seagraves was able to conclude that:

1. The carbon monoxide reaction with Type 304 stainless steel was temperature dependent.

2. Most pronounced effects occurred at temperatures above 1020°F.

3. Destructive effects in polycrystalline 304 stainless steel from exposure to carbon monoxide occurred in the grain boundaries which subsequently led to localized failure of the material.

CHAPTER III

EXPERIMENTAL APPARATUS AND PROCEDURE

The present research program was conducted in two phases. The first was a study of the reactions of carbon monoxide using thin films of iron and nickel and thinned sections of Type 316 stainless steel suitable for analysis by transmission electron microscopy Analysis using transmission specimens rather than replicas was undertaken so that the bulk properties of the materials could be investigated. The second phase was a series of kinetic evaluations of the attack in order to determine the rate of carbon monoxide decompositions and to investigate the carbonaceous deposits occurring on the surfaces and in the grain boundaries.

Apparatus

The apparatus used for preparing vapor-deposited thin films of pure metal and for analysis were either standard or commercial, and are well described in the literature. Therefore, no description need be given in this chapter. Included in this category are:

(a) High Vacuum Deposition Apparatus designed and

constructed by Mr. W. P. Edmondson of the Georgia Tech Engineering Experiment Station

(b) Narda Series 400 Ultrasonic Generator

(c) Rubicon Standard Kelvin Bridge, Catalog Number 1600

(d) RCA EMU 3 Electron Microscope

(e) Bausch and Lomb Research Metallograph, Catalog Number 42-31-36

(f) Phillips X-ray Diffractometer

(g) Perkin Elmer Model 221 Infrared Spectrometer

The apparatus constructed specifically for this work was an electropolisher for preparing transmission specimens of stainless steel and a reactor system for exposing samples to carbon monoxide.

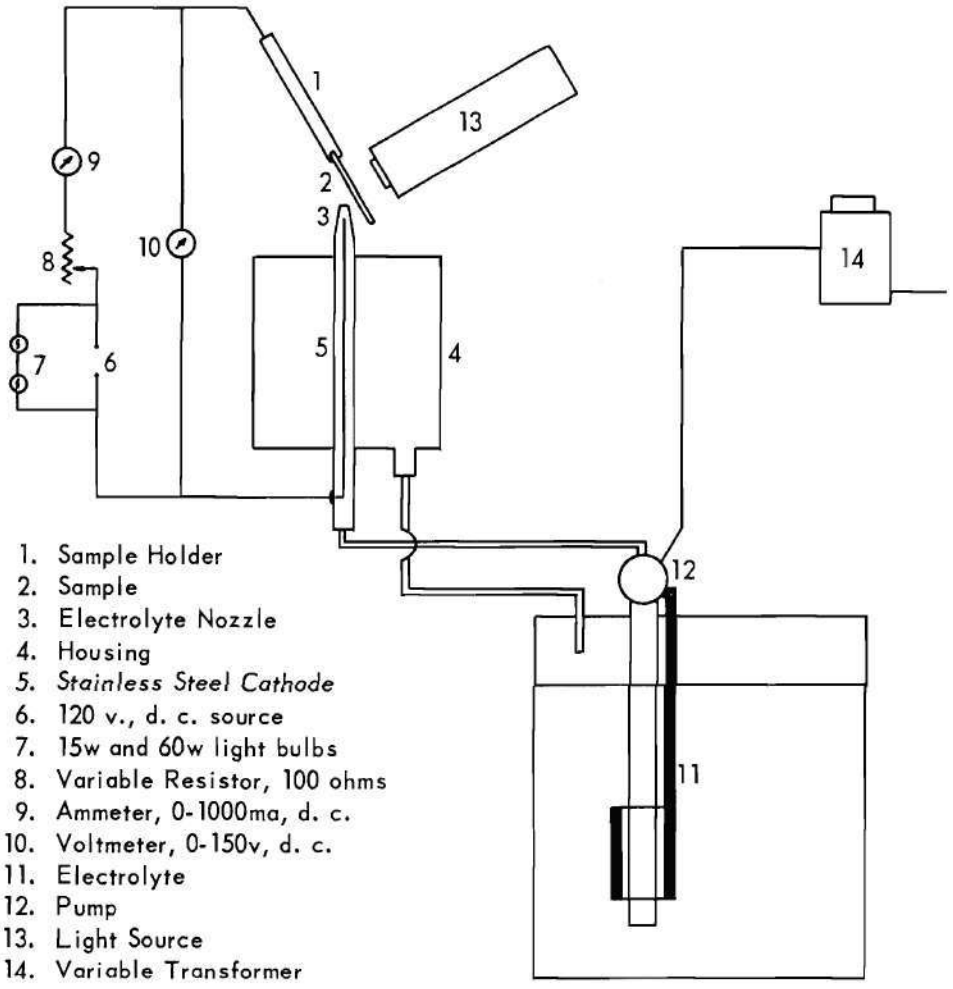
The electropolisher was constructed to prepare sections of stainless steel 1000Å to 2500Å thick from blanks originally about 250 microns thick. The unit is designed to perform a continuous metal removal from a specimen until a fine hole occurs, with the surrounding edges suitable for electron transmission.

The stainless steel blank is approximately two square centimeters in area. It is installed at an angle of 70 degrees to the horizontal and several millimeters above a vertical nozzle. Electrolyte is forced through a nozzle onto

the metal surface. The contact area of the solution on the metal is about 20 square millimeters. Spent liquid is collected in a housing surrounding the nozzle and is returned to a reservoir.

The electrolyte used for polishing stainless steel is a four per cent perchloric acid-amyl alcohol solution, saturated with water. The velocity of the liquid through the nozzle is kept low so that a minimum force is generated on the specimen. Control of this velocity is obtained using a powerstat-controlled fluid pump. A variable position cathode is inserted into the nozzle. A direct current power source is connected to it and to the specimen, which serves as the anode. A direct current generator, capable of delivering 0.27 amperes at 120 volts, is used for the source.

A schematic diagram of the unit is given in Figure 3. Polishing is conducted by bringing the electrolyte in contact with the specimen while maintaining an initial current density of 0.22 amperes per square centimeter. It is reduced to 0.08 amperes per square centimeter after several minutes and maintained until a fine hole appears. Current density is controlled by varying the position of the cathode, which acts to change the total resistance of the electrolyte. The



1. Sample Holder
2. Sample
3. Electrolyte Nozzle
4. Housing
5. *Stainless Steel Cathode*
6. 120 v., d. c. source
7. 15w and 60w light bulbs
8. Variable Resistor, 100 ohms
9. Ammeter, 0-1000ma, d. c.
10. Voltmeter, 0-150v, d. c.
11. Electrolyte
12. Pump
13. Light Source
14. Variable Transformer

Figure 3. Electropolisher for Preparing Transmission Specimens.

hole is readily detected by observing a light beam passing through the polished region. A complete description of the electropolisher and its operation is given in Appendix A.

Fundamentally, the reactor apparatus is capable of providing a controlled exposure of carbon monoxide to both microscopic and macroscopic specimens. The system was designed to operate under steady state gas flow conditions. The exposure zone into which the samples are placed is approximately three inches long by one inch diameter. Heating is done using a tubular furnace surrounding the zone. Temperatures to 1500°F. controllable to within ± 15°F. are possible using a Leeds and Northrup recorder-controller. Operating at 1200°F., the system was successfully run for periods up to 72 hours.

Chemically pure carbon monoxide was used for the experimental work. The minimum purity specified by the manufacturer is 99.5 per cent. Nitrogen, oxygen, and carbon dioxide are the impurities present, occurring in the same proportions as in air. Dry argon was used to purge the system during periods of heating to reaction temperature and subsequent cooling after reaction. Both gases are supplied to the apparatus from high pressure cylinders. The gas flow rates used during a run were approximately 0.3 cubic

foot per hour measured at atmospheric pressure and 70°F. Rate control is accomplished using two stage pressure regulation.

Several accessories were added to the basic unit to ensure optimum reaction condition. A carbon dioxide absorbing filter was installed in the carbon monoxide inlet stream. In order to minimize the temperature gradient through the reaction zone, an additional heater is used to preheat the entrance gas to reaction temperature. Magnesium filings are placed in the forward region of the preheater to remove free oxygen.

The exit gas from the system is forced through an oil bath and is then directed from the experimental area into the open atmosphere. The bath serves to prevent the entrance of air into the system through the exhaust. Flow rates are recorded on the exit side using an inverted, water-filled cylinder. A liquid nitrogen gas trap was connected to the exit side of the furnace just outside the exposure zone in order to trap the gases for subsequent study.

Quartz was used as the construction material for the reaction zone and preheating unit. This was chosen because it is able to withstand high temperatures and because it

does not react with carbon monoxide. Strength properties were not a necessary prerequisite since the system operates at atmospheric pressure. The conduits providing entrance and exit for the gas flow were fashioned from laboratory glass tubing.

A schematic diagram of the apparatus is given in Figure 4. A detailed description of the apparatus and its operation is given in Appendix B.

Experimental Procedure

The experimental procedure employed in this study is as follows. Samples were placed in the reaction zone of the exposure system at room temperature. Wire specimens were precleaned ultrasonically in a xylene medium, dried, and weighed. Argon was fed into the system and, after a 30 minute flush, the reaction zone and preheater were brought to temperature. The specimens were allowed to heat soak for 20 minutes, at which time carbon monoxide was introduced into the system.

At the completion of a run, the carbon monoxide was stopped and argon again flushed through the system. The entire system was cooled to room temperature in the argon atmosphere before the specimens were removed. During

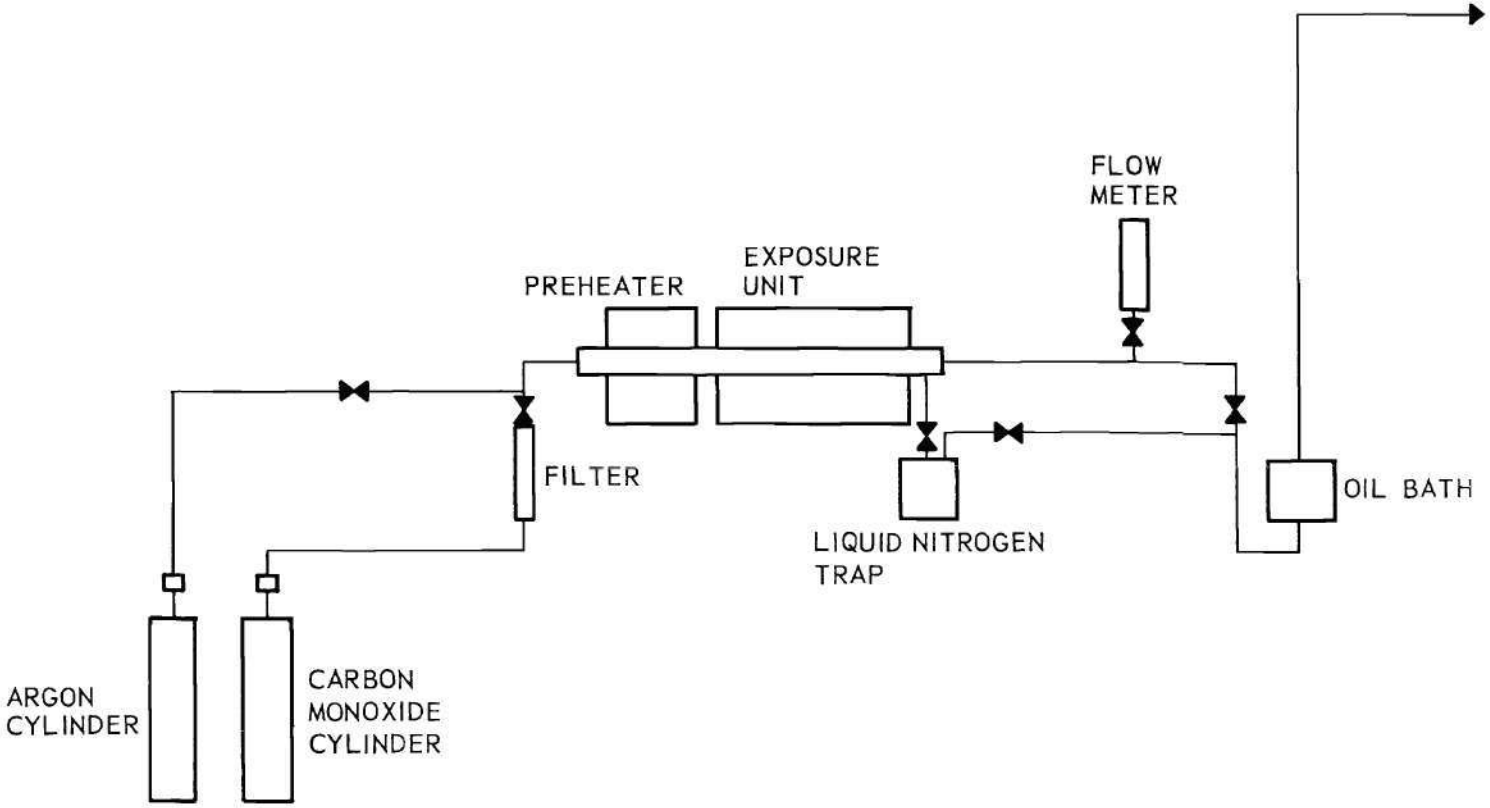


Figure 4. Reactor Apparatus.

operation, periodic flow rate determinations were made. Wire specimens were reweighed after removal from the chamber. They were then ultrasonically cleaned of their deposits and weighed again.

The complete evaluation of the attack was accomplished using electron microscopy, x-ray and selected area diffraction, infrared, resistivity and weight change measurements, and metallurgical analyses. The procedures followed during this evaluation are included, when necessary, in the discussion of results or in the appendices.

CHAPTER IV

DISCUSSION OF RESULTS

Significant results of the high temperature reaction of carbon monoxide with iron, nickel, and AISI Type 316 stainless steel were obtained from 42 of 61 experimental runs. In general, they showed that the reaction of carbon monoxide with iron and stainless steel proceeded through the formation of unstable carbides with a simultaneous or subsequent formation of elementary carbon. Nickel was found to remain inert in the presence of carbon monoxide such that no decomposition to free carbon occurred. Investigation of the rate of reaction of carbon monoxide with Type 316 stainless steel suggested an autocatalytic reaction, dependent on the rate of carbon diffusion into the metal.

The results of the investigation are treated separately for the three metals in order to maintain clarity and allow ease of discussion. The reader is referred to Appendices C-E for the complete results of the investigation.

Iron

The results of the studies involving pure iron showed that its reaction with carbon monoxide at 1200°F. proceeded through the formation of an iron carbide and a simultaneous or subsequent deposition of elementary carbon. The results were obtained from exposure periods of 5, 10, 11, 15, and 18 minutes. Identification of the reaction products was made by electron microscopy and selected area diffraction. Vapor deposited films approximately 1000Å thick were used as the experimental metal. Purity of these films was 99.7 per cent. Impurities were not identified; however, it was assumed that carbon was one of the minor constituents. The operating potential of the microscope for all work was 100,000 volts.

The major constituent present appeared to be the percarbide of iron, $Fe_{20}C_9$, normally identified as Fe_2C, after an initial exposure for five minutes. Selected area diffraction employed to identify the structure could not give a completely distinguishable pattern between the percarbide and a carbide of the type Fe-C reported by Konobejewski (7). The reason for the inability to distinguish between the two was that the transmitted electron beam blacked out the central exposure region where diffraction

above approximately 3.1Å occurs. The diffraction patterns for the percarbide and the Fe-C carbide are very similar except for a strong diffraction at 3.40Å for Fe-C. Since a determination of the existence of diffraction at this value could not be made, the exact structure of the carbide could not be established.

The amount of elemental iron remaining after five minutes was very small in comparison to the original quantity. Diffraction characteristic of iron had a very weak relative intensity, which indicated that the specimen had almost been totally transformed.

The form of the carbon deposits after five minutes reaction appeared as extended growths which were semicontinuous on, and away from, the metal surface. This is shown in Plate 2, Figure C. The origins of these depositions could not be determined; however, it appeared as though the grain boundaries or dislocations served as nucleating points. Several grain boundaries, in particular, had increased to thicknesses of approximately 0.01 micron due to carbon deposition. Particles were observed in the extended ends of the deposits and ranged in size from 0.02 to 0.1 micron. Davis, Slawson, and Rigby (3) observed similar particles in carbonaceous regions on iron

exposed to carbon monoxide. They tentatively identified these as particles of iron percarbide, $Fe_{20}C_9$, which acted as nuclei for filament growth of carbon. Contrary to their observations and observations of Hofer, Sterling, and McCartney (8), the particles observed in this investigation were not primarily at the ends of filament-type growths of the same thickness, but were also at the ends of growths which were on the order of five times as thick. This indicated that, if the particles were catalyzing nuclei of carbide, they were free to move randomly rather than unidirectional as previously supposed, or that, in addition, carbon already present also promoted decomposition. The possibility that the particles were folds at positions where carbon filaments had broken was considered, but rejected after close scrutiny revealed no indication of any growth beyond these points.

The continued reaction (i.e. exposures for 10, 11, 15, and 18 minutes) resulted in a total transformation of iron to iron carbide and a continued deposition of elementary carbon, as shown in Plates 3 and 4, Figure C-1. The structure of the carbide after 15 minutes exposure did not appear identical to the carbide which was present after five minutes. However, a positive identification was not made

due to the limitations of the diffraction apparatus as explained previously. That the carbide was not the same for long exposures as after the five minute exposure indicated that a transformation or partial transformation between carbides occurred.

The continued deposition of carbon took place primarily on existing growths with only minor new nucleation in other regions. For longer exposure times the presence of iron could not be detected, which strongly suggested that the reaction to yield carbon was catalyzed either by the carbide or by other nuclei of carbon, or both. Observations further showed that the carbon growths had increased to several microns in length in a three dimensional dendritic pattern. Thicknesses of these growths, in some cases, were as large as 0.3 micron. Particles remained approximately the same size as previously mentioned. These observations indicated again that the supposedly catalyzing particles were not the only catalysts, but that the resulting carbon also activated further deposition.

A very limited investigation was made to compare the reaction of oxidized iron specimens with carbon monoxide at 1200°F. to the reaction with pure iron. Specimens

identical to those used in the above investigations were first oxidized for one minute at 1200°F., then subjected to carbon monoxide for five minutes. The results showed that the reaction with carbon monoxide to form elementary carbon either exhibited a prolonged incubation period or did not react in a similar fashion to pure iron at all. Due to limited time diffraction was not employed; however, observations of the exposed specimens gave no indication of a deposition of carbon. Grain boundaries and dislocations likewise showed no evidence of attack. Assuming that the one minute exposure to air oxidized the thin film specimen completely or nearly completely to Fe_2O_3, the observations appeared in excellent agreement with the work of Juliard, Rayet, and Ludé (2), who postulated that the reaction to form elementary carbon does not begin until the reduction of the oxide through Fe_3O_4 and FeO is completed to an extent that free iron exists.

Nickel

The results of the investigation of nickel subjected to carbon monoxide at 1200°F. indicated that nickel, in the thin film form used for this study, did not react with nor catalyze the decomposition of carbon monoxide. The study

was made in a similar manner to that of the investigation of iron. Electron microscopy and selected area diffraction were used for analyses. The operating potential of the microscope was 100,000 volts. As with iron, vapor deposited films were used as the experimental metal. Specimen purity was 99.7 per cent; impurities were not identified. Seven experimental runs were made for periods of 1, 2, 5, 7, 15, and 45 minutes.

Observations of the subjected specimens are given in Plates 2-4, Figure D. All showed no carbon deposition nor any semblance of reaction as would be evidenced by particle development or dislocation or grain boundary attack. The observations from the specimen exposed for five minutes did show a particle-like deposition scattered randomly across the surface. However, it had been necessary to store this specimen, and two others, which had been subjected to carbon monoxide for two and seven minutes, in a dessicator for almost a week before any microscopy or diffraction work was undertaken. Since it was observed that the particle distribution and appearance was the same in all cases, it was assumed that dust or dirt had deposited on the specimens. Selected area diffraction positively identified the structure of each to be solely nickel. An exposure period of 45

minutes was made to ascertain whether a reaction with carbon monoxide could occur after a prolonged "incubation" period. The results, as obtained by electron microscopy, again showed that no carbon forming reaction had occurred.

An investigation was made in the same manner as with iron to determine the effect of oxidizing the nickel specimens for one minute prior to subjecting them to carbon monoxide. Experimental runs were made for 5 and 15 minutes. No reaction to form elementary carbon occurred. Selected area diffraction used to identify the structure showed the presence of nickel and nickel oxide after five minutes and only nickel after fifteen minutes.

AISI 316 Stainless Steel

The reaction of carbon monoxide with Type 316 stainless steel at 1200°F. was investigated first by electron microscopy and selected area diffraction as in previous iron and nickel studies. A second investigation using wire specimens was made to investigate the kinetics of the reaction.

The results obtained by electron microscopy and selected area diffraction showed that the reaction proceeded similarly to that with iron in that carbon monoxide reacted with the metal to form a carbide or carbides with a simultaneous or

subsequent deposition of elementary carbon. Specimens on which observations were made were exposed at a carbon monoxide pressure of 50 microns of mercury in order to retard the reaction and thus be able to better observe the initial effects. This was accomplished by connecting the exposure chamber to a vacuum system and proceeding in the same manner as for standard runs. The specimens were electrothinned to approximately 1000Å to 2000Å by the procedure given in Appendix A. The carbon content of the prepared specimens was determined to be 0.06 per cent.

Observations after exposures for 2 and 5 minutes showed that carbon deposition began at dislocations and grain boundaries (Plates 2 and 3, Figure E-1). The deposits were similar to those found on iron except that no particle formation was detected. Additional formation took place primarily on existing deposits although some minor depositions occurred on the entire surface. Numerous stress-induced dislocations caused by cold reduction of the original sheet to 0.010 inch thickness were present in the specimens and it was not possible to determine whether the deposits on the matrix surface were initiated at these faults. These numerous dislocations could also be the reason why no particles in the growths were observed, since distinguishing

between the two would be difficult.

Selected area diffraction of specimens exposed to carbon monoxide at one atmosphere pressure showed that the reaction had proceeded to an extent that the entire austenite lattice was transformed after one minute. Idenitfication of reaction products for an entire series of exposures of 1, 2, 5, and 10 minutes was inconclusive insofar as defining an exact structure. The results obtained are given in Appendix E, Table E-1. It is suggested that carbides of the type Fe-C, $Fe_{20}C_9$, Fe_3C, $(Cr,Fe)_7C_3$, $Cr_{23}C_6$, and Mo_2C were present. The reasons for this broad identification are that the diffraction patterns for the above compounds are very similar except in the blacked-out region of the transmitted beam and because many weak diffraction lines were not observed clearly enough that corresponding interplanar spacings could be calculated.

Evaluations of the kinetics and mechanism of reaction were accomplished using wire samples of Type 316 stainless steel prepared in the manner given in Appendix B. Eighteen experimental runs were made for exposure periods from 1-72 hours. The results, shown entirely in Appendix E, in general suggested that the reaction was autocatalytic, dependent on the rate of decomposition of unstable reaction products and

on carbon diffusion into the metal. Metallurgical examinations made during the course of work further showed that metal loss from surface regions occurred after prolonged exposures and that the deleterious effect in the metal was due mainly to formation of carbides in the grain boundaries.

Fifteen runs were made for exposures from 1-35 hours in order to measure the changes in weight of the samples due to carbon addition with time. The results are shown graphically as the solid line in Figure 5. The curve was fitted to the measured values by the method of least squares data fitting process. The data show that the rate of reaction proceeded exponentially at first then decreased to an almost linear gain after approximately nine hours. A mathematical expression for the increase was not formulated since it would be a polynomial expression of the form

$$I = A_1T^1 + A_2T^2 + A_3T^3 + \ldots$$

where, I = weight increase

$A_1, A_2, A_3, \ldots$ = constants

T = time

and would not add to the physical significance of the shape.

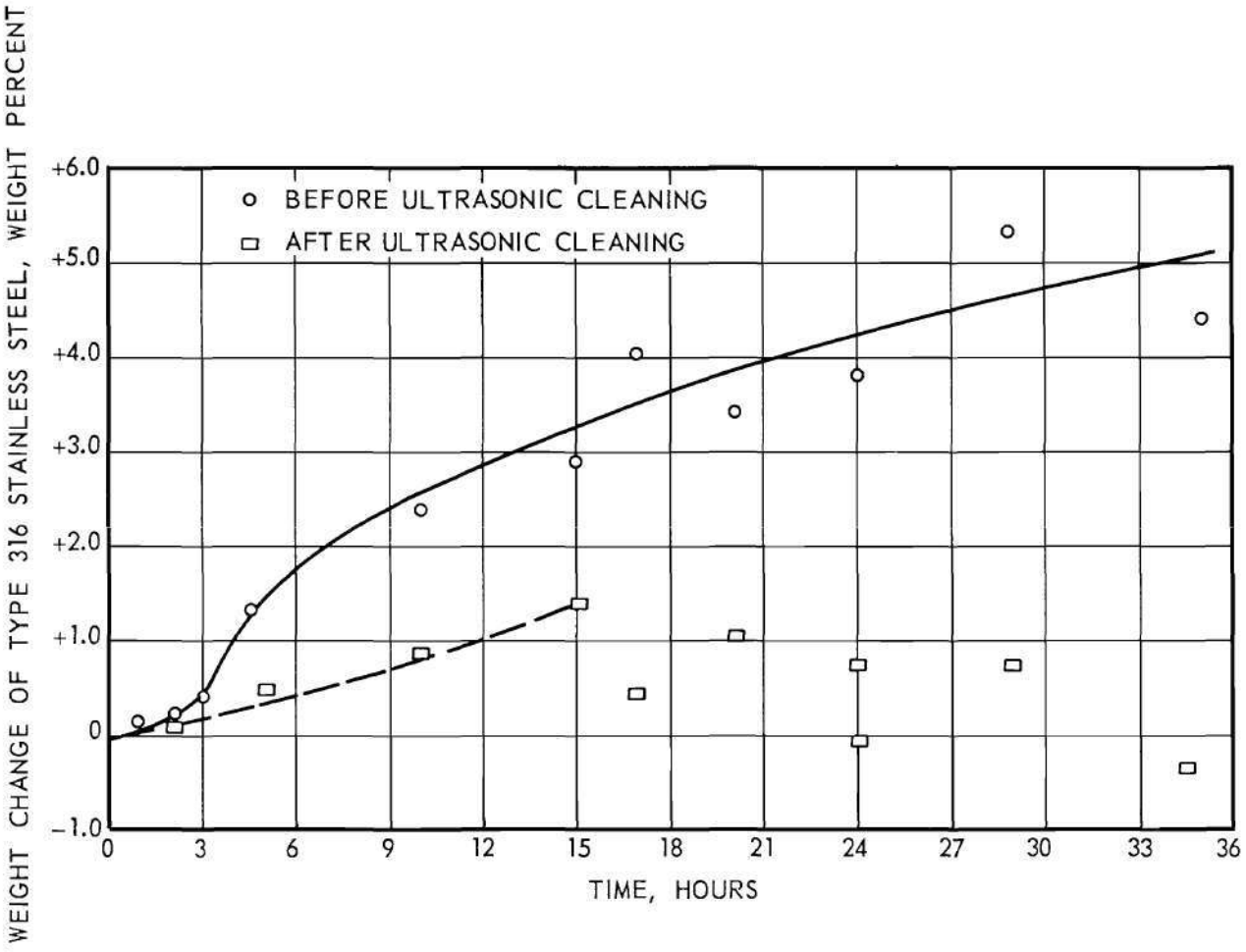


Figure 5. Weight Change of Type 316 Stainless Steel from Exposure to Carbon Monoxide at 1200°F.

The approximate rate of weight increase with time was calculated from the slope of the weight increase curve and is shown in Figure 6. These results show that the rate increased continuously to a maximum at about 3.6 hours then decreased exponentially to an almost constant value at approximately 12 hours. Both curves have forms corresponding to those for autocatalytic reactions. The data obtained from Runs 7B, 8B, 9B, 15B, 16B, 17B, 18B, 19B, 23B, 31B, and 32B further showed that the weight increase can be related in a manner similar to diffusion-controlled processes as weight gain proportional to the square root of time. This is shown graphically in Figure 7.

Carbonaceous deposits on the wire samples were observed to have definite filament-like growths and were determined by x-ray diffraction to be composed of graphite and metal or metal carbides of iron, nickel, and chromium. A positive identification of metallic structures could not be made because the presence of graphite decreased the intensities of the other diffraction lines and because numerous weak lines were apparently lost in the noise level of the instrument. Besides graphite, the diffraction patterns most strongly suggested the presence of cementite, Fe_3C. The graphitic carbon was burned from the deposits and the resulting oxides were

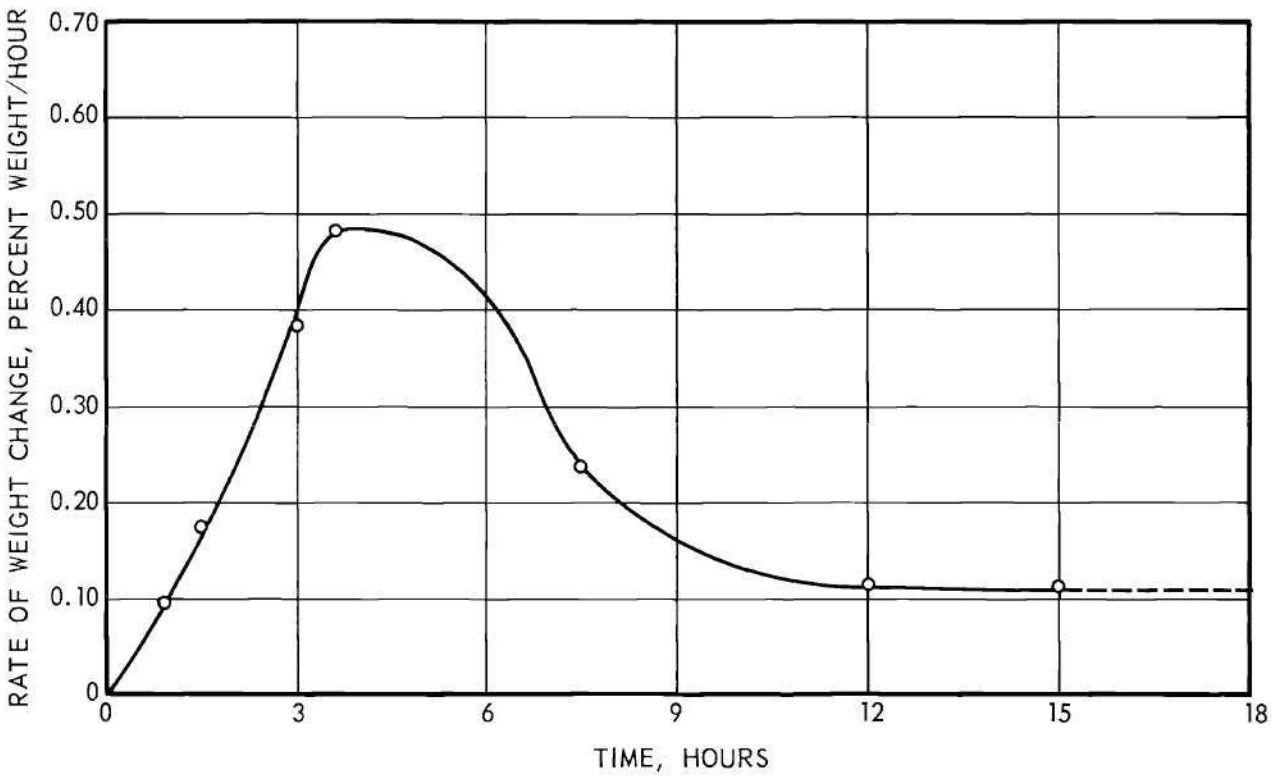


Figure 6. Rate of Weight Change of Type 316 Stainless Steel from Exposure to Carbon Monoxide at 1200°F.

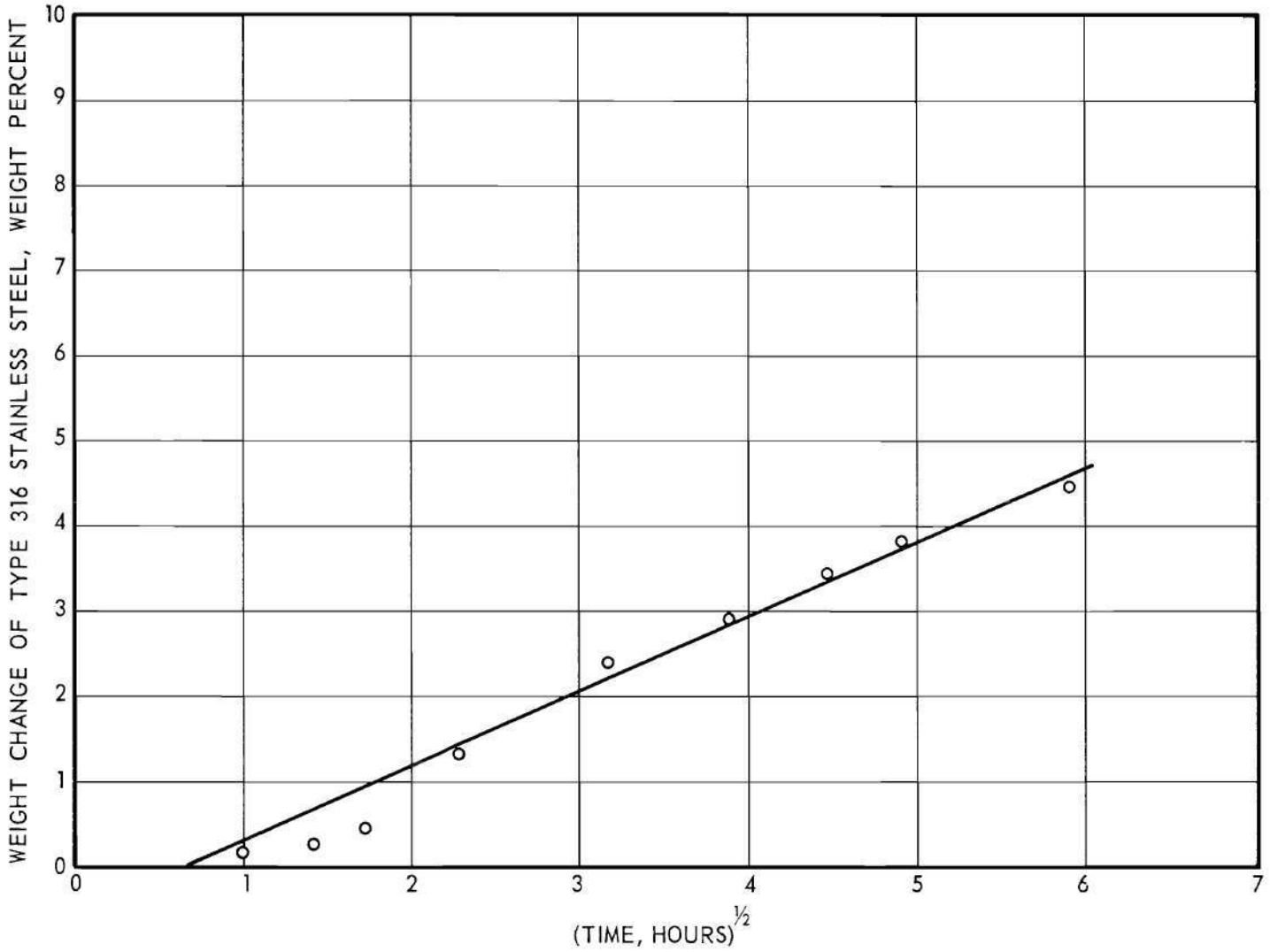


Figure 7. Weight Change of Type 316 Stainless Steel from Exposure to Carbon Monoxide at 1200°F versus Time$^{1/2}$.

analyzed for iron. Calculated on the basis of pure metal, it was found that 28 per cent of the total deposits were iron. Qualitative Borax bead tests indicated an absence of nickel but showed a small amount of chromium. Since the diffraction patterns of the deposits did not suggest the presence of a body-centered cubic structure (which would have been the case had free iron been present), it was realistic to believe that the deposits were primarily graphite and an iron carbide.

The above results strongly indicate that the reaction proceeded through the formation of an iron carbide. It is well known that the iron carbides are unstable at elevated temperatures and atmospheric pressure; therefore, it appears that an autocatalytic effect was created by the formation of iron carbide which subsequently decomposed back to free iron and carbon. The decrease in reaction rate after three and a half hours indicated that one or both reactants were almost all comsumed; but, because the carbon monoxide concentration was held constant, it can be concluded that iron was the limiting reactant, based on iron-carbon monoxide interaction.

Metallurgical examination of reacted wires showed that carbon had diffused completely through the grain boundaries

after five hours exposure. Diffusion into the matrix was detected by several examinations yet to be discussed but was not observed even after 72 hours exposure. This indicated that carbon remained in solution or was tied up as molybdenum carbide, Mo_2C, which is so finely dispersed that its presence cannot be detected by optical microscopy. A single investigation was made to determine if the grain boundary phenomena after five hours was caused by precipitation due to carbon present in the original wire. Examination of a sample heat treated for 5 hours at 1200°F. in argon and allowed to air cool showed a slight precipitation, much less than for the sample treated in the same manner in the carbon monoxide atmosphere.

Diffusion data for carbon into the stainless steel matrix was unavailable. Selected area diffraction showed that the matrices of transmission specimens were completely transformed after exposures of one minute. Considering that the total transformation of those specimens in one minute was caused by carbon diffusing through thicknesses of approximately 2000Å, then, by a linear approximation, the time required to diffuse carbon through the austenite of the wires should be on the order of 10 hours. Resistance data, discussed below, showed that diffusion actually was faster.

The electrical resistance of Type 316 stainless steel wire during exposure to carbon monoxide at experimental conditions was measured in order to determine the resistance change caused by reaction. Wire samples were prepared in the manner given in Appendix B. Three runs were made for 10, 19, and 72 hours. The results are shown graphically in Figure 8. The curves shown are for individual wire for each run based on an average value of the total number of wires in each exposure. Resistances at zero exposure time do not coincide because the lengths of the wires were not identical.

The results showed that the resistance of the wires increased continuously to a maximum at approximately 2 to 3 hours, then decreased to a resistance value less than the original at about 6 hours. An attempt was made to quantify the data; however, it was abandoned due to extremely limited information on resistivities of the possible resulting carbides.

The rate of change of resistance with time was obtained from the slopes of the curves in Figure 8. These are shown in Figure 9. It is shown that the maximum rate of increase in resistance occurred after approximately 1½ to 2¼ hours exposure and that the maximum rate of decrease in resistance occurred after approximately 3½ to 5 hours. Interpreted

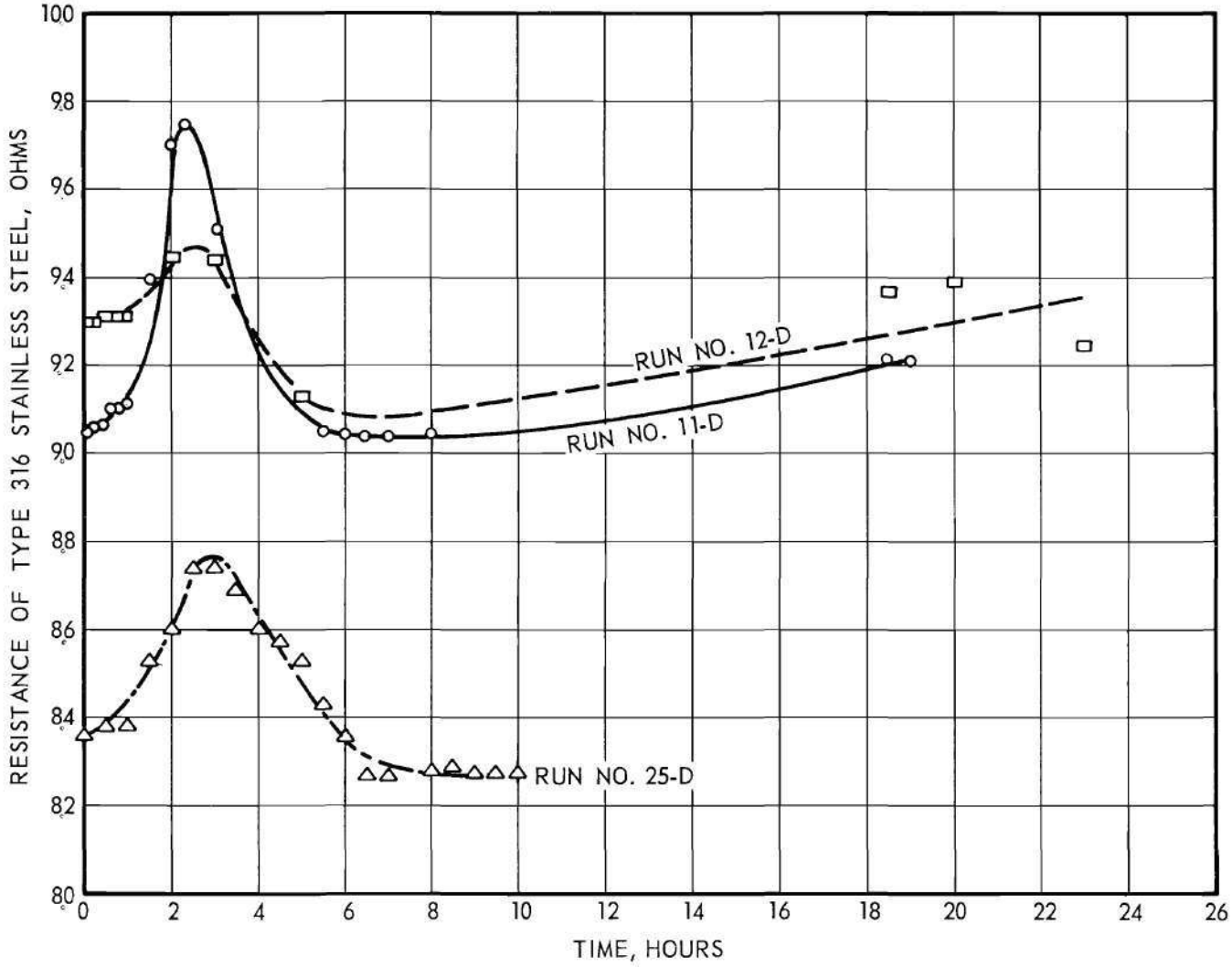


Figure 8. Electrical Resistance Change of Type 316 Stainless Steel During Exposure to Carbon Monoxide at 1200°F.

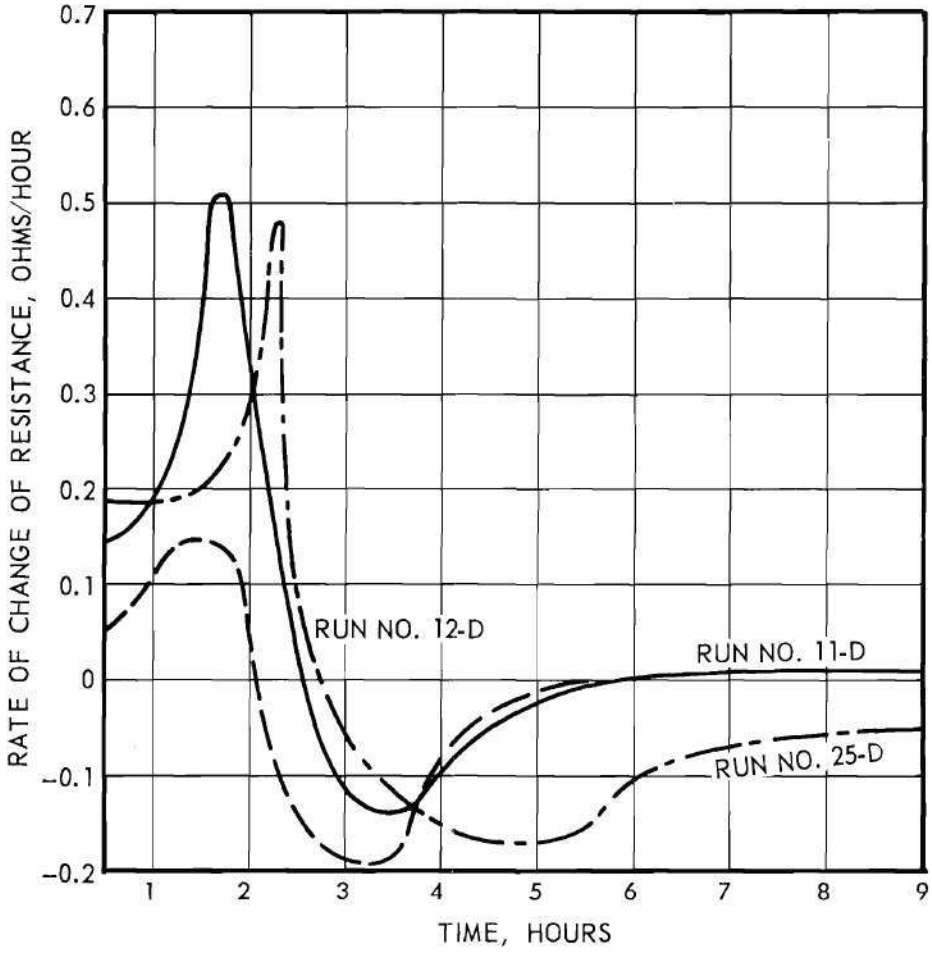


Figure 9. Rate of Electrical Resistance Change of Type 316 Stainless Steel During Exposure to Carbon Monoxide at 1200°F.

according to the postulate set forth to explain the weight change data, the maximum rates of increase and the maximum resistances are due to diffusion of carbon from decomposition of unstable carbide into the metal. The maximum rates of decrease and the minimum resistances are due to the formation of carbon on the surface. This certainly appeared reasonable since surface deposits would act as parallel resistors and decrease the total resistance of the sample. The time positions of the maximas and minimas contribute to the postulated reaction a basis for the autocatalytic appearance of the weight data. Initially, carbon monoxide reacted on the metal surface to form unstable carbides, which decomposed and allowed carbon to diffuse inward. This corresponded to an increased resistance of the metal while the reaction still proceeded at the same rate because metal remained freely available on the surface. When the carbon concentration gradient in the metal had decreased sufficiently so that immediate diffusion of carbon from the surface could not occur, the formation of carbide increased until the surface metal was consumed. This was indicated by the maximum rate of decrease in resistance occurring just before the reaction rate decreased.

A theoretical approach to the postulated reaction

contributes the reason for continued carbon deposition after the elemental metal reactant from the surface was consumed. The following discussion is based on experimental indications that the reaction formed Hagg carbide, Fe_2C, according to

$$2Fe + 2CO = Fe_2C + CO_2.$$

At 1200°F., the free energy of decomposition of Fe_2C is -2500 calories per mole (9). The equilibrium constant was calculated to be 3.151 mole using the expression

$$\Delta F = -RT\ln K$$

where ΔF = free energy of decomposition, calories per mole

R = gas constant, 1.987 calories per mole per °K

T = temperature, °K

K = equilibrium constant

$\ln$ = natural logarithm.

For the decomposition of Fe_2C according to the equation

$$Fe_2C = 2Fe + C,$$

equilibrium conditions will exist such that

$$3.151 = \frac{[Fe]^2 [C]}{[Fe_2C]}$$

where [ ] indicates concentration.

The solution to the equation, based on one mole of Fe_2C dissociating, indicates that equilibrium is achieved when the concentration of iron is 1.33 mole. This iron-iron carbide equilibrium suggests a probable means for renewing the depleted quantity of reactant and also explains a mechanism by which carbon addition to the metal can continue. Further considerations show that continued carbon deposition will force the equilibrium to iron carbide and thus decrease both the amount of iron available to react and the rate of weight gain, as expressed by the parabola weight form in Figure 7. Additional theoretical approaches of this type show also the possibility of carbide transformation to a more stable form, Fe_3C, for example.

The reacted wire samples, from which deposits were ultrasonically removed, were reweighed in order to investigate the weight gain in the metal. The results are shown as the broken line and as the recorded points labeled "after

ultrasonic cleaning." It was difficult to assess the amount of experimental error in these measurements since definite removal of the deposits could not be verified. The values were obtained by cleaning the specimens ultrasonically, weighing, and repeating the process until a constant weight was obtained. The measured values up to 15 hours showed a continuous weight increase, but thereafter, the values became random. The points above 5 hours, except for the two which indicated a weight loss, show some resemblance to a constant value. An average increase was calculated and found to be 0.84 per cent, or 0.042 grams based on a 5 gram metal sample. Weight losses caused by metal removal were observed in several instances; thus, the measurements lose their significance insofar as explaining the diffusion of carbon during reaction for long periods of time. They do show a definite increase in weight from carbon diffusion for shorter times.

In summary of the above observations and data on the reaction of carbon monoxide with Type 316 stainless steel at 1200°F., it is suggested that the following was the mechanism of reaction:

$$2Fe + 2CO = Fe_2C(\text{unstable}) + CO_2$$

$$Fe_2C = 2Fe + C(\text{into metal})$$

$$2Fe(\text{from previous decomposition}) + 2CO = Fe_2C + CO_2$$

$$Fe_2C = 2Fe + C(\text{on surface}).$$

Reaction rates for autocatalytic reactions are given as a logarithmic expression involving an original concentration of product. The rate was not formulated for this reaction since no numerical value can be assigned to the original product concentration.

The gaseous reaction products from Runs 4B and 17B were quenched to -192°C. in liquid nitrogen after specimen exposure for 5 hours in order to determine by infrared spectroscopy whether unstable carbonyls of iron or nickel were formed during the reaction. The results showed that no carbonyls were formed during the reaction or, if they were, they formed as an activated complex of extremely short life such that decomposition took place before reaching the cold trap. Carbon dioxide was the only identified reaction product. An unusual infrared absorption pattern was obtained for the exit gases which could not be completely resolved. Carbon monoxide and carbon dioxide type bonding were definately established as being present. Absorption which

occurred at approximately 2.64, 2.72, 3.30, 3.44, 8.37, 8.45, 8.70, 8.95, and 9.05 microns could not be associated with any normal bonding. Characteristic absorption for water, which is almost always a gaseous contaminant, did not occur. The best explanation is that bonding of the acetylene type was present. Carbon suboxide, C_3O_2, has an absorption pattern (10) similar to that obtained, but numerous additional absorption peaks for this compound could not be observed. Spurious bonds which have been identified by the Perkin Elmer Corporation (11) can account for all of these unidentified peaks but it seemed highly unreasonable that identical spurious bonds would occur in the spent exit gases while none could be detected in carbon monoxide standards obtained in the same manner. It was thought that xylene, which might have remained on the specimen's surface from initial cleaning and subsequently quenched in the trap, could produce the unusual absorption. However, two attempts to reproduce the data using xylene-carbon monoxide mixtures failed to duplicate the experimental results. It is necessary, therefore, to report that identification of gaseous reaction products was inconclusive, in part.

Metallurgical examinations of specimens which were used to obtain the rate of reaction showed carbide precipi-

tation in the grain boundaries after 5 hours. Additional observations showed that metal losses occurred in surface regions. The losses were nonuniform sections of individual grains, although the examinations did not rule out the possibility of complete grain removal. The surface attack after 72 hours exposure indicated a loss in metal to a depth of about 3 microns from grains approximately 0.8 square millimeters. Metal loss of this form, or of some similar form is suggested to be the reason for weight loss of specimens after ultrasonic cleaning. The only apparent reason for the loss is that the ultrasonic vibrations during cleaning were sufficient to cause fatigue in these areas. Fracture of the sample exposed for 72 hours occurred in the grain boundaries because of carbide precipitation. The composition of carbides in the grain boundaries was not determined. It is presumed that they were $(Cr,Fe)_{23}C_6$, since this is the normal grain boundary carbide occurring in stainless steel after heating to 1200°F (12).

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

From this research work it was concluded that:

1. The reaction of carbon monoxide and iron at 1200°F. proceeded through the formation of an unstable iron carbide, suggested to be the percarbide, $Fe_{20}C_9$. It is further suggested that this carbide most likely formed from the carbon monoxide-iron surface reaction as dictated by activated complex theory.

2. Pure nickel did not react with nor catalyze the decomposition of carbon monoxide at 1200°F.

3. Nickel oxide was reduced to pure nickel by carbon monoxide at 1200°F. without accompanying reactions.

4. The reaction of carbon monoxide and Type 316 stainless steel at 1200°F. proceeded through the formation of metal carbide or carbides. It is suggested that the reaction proceeded through the formation of iron carbide.

5. The rate of reaction of carbon monoxide with Type 316 stainless steel at 1200°F. passed through a maximum at a finite time after initial exposure. It is suggested that the reaction was autocatalytic in nature.

Recommendations for Further Research

It is recommended that the kinetics of reaction of carbon monoxide with pure iron be investigated in the temperature range of 1000°F. to 2000°F. This investigation should be carried out using an exposure system in which the concentration of carbon monoxide can be controlled. The use of a thermobalance would enable continuous measurements of metal weight gain during exposure. Two samples, identical in all respects, but different in dimensions, should be used to show diffusion dependency.

Further investigations of the carbon monoxide reaction with stainless steel at temperatures in the range of 1000°F. to 2000°F. should be made in accordance to the following:

1. Identification of solid reaction product or products. Type 304 ELC would eliminate the complexity caused by additional alloying elements. Transmission specimens exposed at low carbon monoxide pressures would enable identification of reaction product or products by electron microscopy and selected area diffraction before complete transformation of the lattice. X-ray flourescence could also be used to distinguish between similar carbides.

2. Evaluation of kinetics. Type 304 ELC should

also be used for this investigation. It is suggested that the evaluation be carried out simultaneously or after the investigation with pure iron. The procedure recommended for this study is identical to that for pure iron.

3. Identification of possible gaseous reaction products. The infrared studies in this program were very inconclusive. It is advisable that these be continued in the same manner. To enhance the identification, quantitative analyses should be made to determine the exact compounds.

APPENDICES

APPENDIX A

AN ELECTROPOLISHER FOR PREPARING STAINLESS STEEL TRANSMISSION SPECIMENS

The electropolishing technique to produce stainless steel specimens for electron microscopy was employed in this research program so that the effect of carbon monoxide on the bulk properties of the alloy could be studied. The polishing unit was designed similarly to the one used by Washburn (13) to prepare thinned sections of cleaved magnesium oxide crystals. This design was not selected until a series of trials using other standard polishing methods failed to give satisfactory results.

The basic unit is comprised of three major components; an electrolyte reservoir, a controlled direct current circuit between the electrolyte and the specimen, and an electrolyte-specimen contact assembly. These components, as employed in the system, provide the following capabilities which were considered essential for controlled metal removal:

(a) a controlled electrolyte flow rate,

(b) a controlled current density,

(c) a variable potential,

(d) a limited specimen-electrolyte contact area,

(e) a controlled electrolyte temperature, and

(f) a visual observation of the metal removal process.

The electrolyte reservoir is a 3000 milliliter Pyrex beaker into which a Bronwill Scientific controlled temperature fluid pump was installed. The pump is connected to a variable transformer so that its discharge rate can be varied. A General Electric Type SA motor to which a General Electric Type SD generator was connected serves as the direct current power source. This unit is capable of delivering a direct current of 0.27 ampere at 120 volts to the system. A 100 ohm variable resistor and a zero to one direct current ammeter are installed in the positive line from the generator to control and measure the current to the system, respectively.

The specimen-electrolyte contact unit consists of an enclosed vertical jet nozzle above which the specimen is mounted. The nozzle is 4 inches long and 1/8 inch in diameter, tapered to 1/32 inch diameter at its upper end. The enclosure is 3 inches high, 2½ inches in diameter and has a ¼ inch exit port in the bottom. The entire assembly is made of glass. The nozzle is raised 3/4 inch above the housing to allow ease of operation. A 0.010 inch diameter

stainless steel wire was inserted into the nozzle from beneath its housing. This wire serves as a cathode and is sufficiently long to reach the nozzle outlet. The pump is connected to the nozzle inlet by a 1/8 inch Tyflon tubing. A 1/4 inch tube is attached from the exit port of the enclosure to the reservoir and serves to recycle the electrolyte.

The specimen, approximately two square centimeters in area, is mounted several millimeters above the nozzle at an angle of 70 degrees from the horizontal. The mount is a stainless steel tweezers, six centimeters by one centimeter, which clamps the specimen in position. The positive electrical lead from the generator is connected to the specimen clamp and the negative lead to the stainless steel cathode located in the nozzle. A 0 to 150 direct current voltmeter is connected between the specimen and the cathode. Number 16 copper wire is used to provide the external leads.

The operating conditions for the unit were all determined by trial and error based on suggestions by Thomas (14). The electrolyte found most effective was a four per cent perchloric acid-amyl alcohol solution, saturated with water. No electrolytes which contained acetic acid were tried because of their explosive characteristics. Electrolytes containing hydrochloric acid were found to burn or pit the

specimens during polishing at high current densities. The A-2 electrolyte used in the Knuth system gave satisfactory results; however, the solution had to be renewed daily and created a problem of material wastage.

The optimum position of the specimen was obtained in a straightforward manner. It was observed that, at distances greater than about one centimeter from the nozzle and cathode the area polished was too large to produce a fine hole through the specimen. Distances less than about two millimeters caused excessive burning. Between these limits, polishing proceeded satisfactorily in an area of about twenty square millimeters. The inclined position of the specimen was used so that the current density would be decreasing perpendicular to the surface at the point of electrolyte contact. This serves to retard the rate of polishing through the specimen while thinning an enlarged contact area.

For the electrolyte used, room temperature was satisfactory. During periods of rapid polishing, the temperature of the electrolyte at the point of contact would increase as much as 50°F.; however, the use of the large reservoir acted as a heat sink and maintained essentially room temperature.

The determination of the proper current density was done by plotting the rate of polishing versus current density. The rate of polishing was calculated by recording the time required to produce a hole in the specimen blank originally 0.010 inch thick. This calibration is shown in Figure A-1. For preparation, an initial current density of 0.22 amperes per square centimeter was maintained for the first three minutes to achieve a rapid polish. If a hole did not appear during this phase, the current density was reduced to 0.08 amperes per square centimeter. The polishing was continued at this rate until a hole through the specimen could be detected. This slow rate of polishing was used during the final preparation so that the operator would have sufficient time to react to the appearance of a hole and stop the operation. A simple calculation, based on a spherical metal removal from the specimen at a current density of 0.08 amperes per square centimeter gives a reaction period of 0.71 seconds for the operator to stop the polishing before the thickness of the edges exceeds 2000Å. If a hole had appeared during the first stage, the specimen was discarded. A light source taken from a Leitz metallurgical microscope was mounted directly behind the specimen so that the hole could be detected by observing the appearance

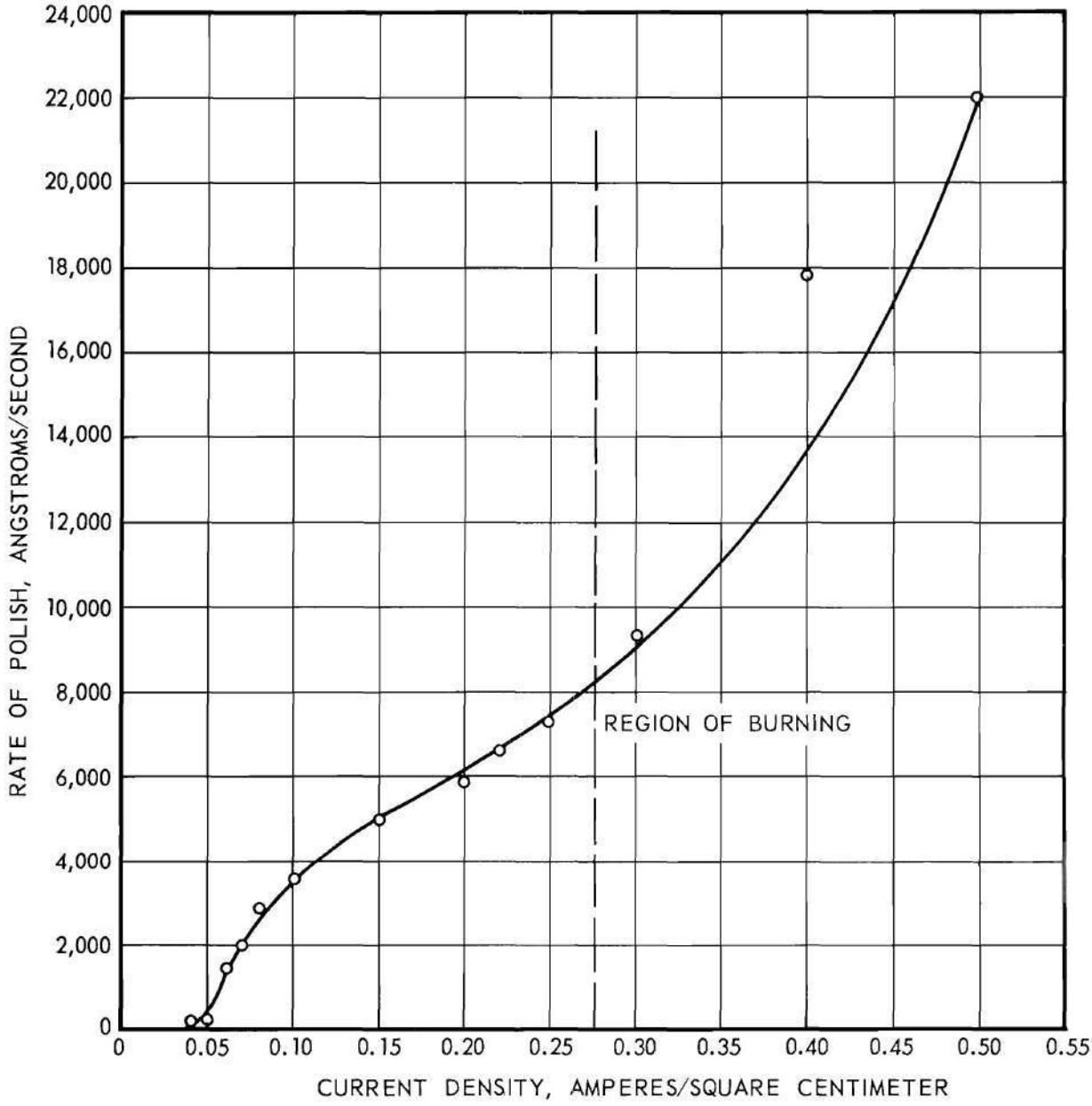


Figure A-1. Rate of Electropolishing.

of the light beam through the metal. The flow rate of electrolyte was kept as low as possible so that the pressure created by the liquid could not break the thinned sections surrounding the hole. Once a hole was detected, the polishing was stopped. The specimen was then washed in ethanol, dried, and placed in a dessicator. Prior to further work, the specimen was cut to 3/8 inch diameter to fit the holder of the electron microscope. The prepared specimens were checked by microscopy to determine whether suitably thinned sections existed. Successful preparations were achieved about once in ten tries. Figure E-1, Plate 1, shows a thinned section of Type 316 stainless steel.

APPENDIX B

REACTOR APPARATUS AND EXPERIMENTAL PROCEDURE

Apparatus

The primary criterion for the design of the reactor apparatus was to provide a controlled exposure of carbon monoxide to micro- and macroscopic specimens at 1200°F. Operating conditions and control features for such a system were selected based on the work of Seagraves (see Chapter II). From his work, high purity carbon monoxide was selected for the experimental gas in order to avoid extraneous effects of contaminants. Also, for the temperature range 1000°F. to 1300°F., the reaction $2CO = CO_2 + C$ was shown to be very temperature dependent. Rigid temperature control seemed important since the program was established to study the effect of carbon monoxide at 1200°F. For an apparatus designed to use a replenishing supply of experimental gas, a steady state gas flow system using flow rates less than one cubic foot per hour was suggested.

The reactor apparatus designed using these suggestions and considerations is shown in Figure 4. As shown

the basic components are (a) filtered gas supply, (b) preheating element, (c) reaction chamber, and (d) exhaust system.

The experimental gas used is chemically pure carbon monoxide. The minimum purity specified by the manufacturer is 99.5 per cent. Impurities present are nitrogen, oxygen, and carbon dioxide. Dry argon is supplied to the system to create an inert atmosphere during periods of heating and cooling so that oxidation of the specimens will not interfere with the experimental results. Both gases are contained in high pressure steel cylinders. The gas outputs are controlled by two-stage pressure regulators. Needle valves control the flow rates through the exposure zone. An Ascarite filter is employed through which the carbon monoxide is passed before contacting the metal specimens to remove carbon dioxide from the experimental gas. A dual entrance stopcock prevents simultaneous flow of both gases.

The preheating element and the reaction chamber are classified separately because of the function each performs. Both are contained within a 26 inch quartz tube, one inch in diameter. The material choice for quartz was made because of its satisfactory high temperature properties and because it is inert to carbon monoxide. Since the

system is operated at atmospheric pressure, strength properties were not considered.

The preheating unit is located three inches from the inlet end of the tube. The heating region is seven inches long. During operation, the entering gas is heated to reaction temperature before passing over the experimental samples. In this manner, the temperature gradient through the exposure zone is reduced to a satisfactory tolerance. Magnesium filings are inserted in the forward region of the unit to remove oxygen from incoming gases.

The reaction chamber is positioned three inches from the tube exit and extends eleven inches. The chamber has a three inch zone in which the temperature is constant. A discussion of this zone is given below. For experimentation using transmission specimens, a copper palate, two inches long, 3/4 inch wide, and 1/16 inch thick, is used as a specimen holder. The palate is inserted into the reactor chamber manually while the system is at room temperature.

The preheating unit and reaction chamber are heated by commercial, tubular furnaces, manufactured by the Fisher Scientific Electric Company. The enclosed heating regions are 1¼ inches in diameter Heating is accomplished by

electrical resistance using nichrome wire. The maximum operating temperature for the furnace is 1800°F. The pre-heating furnace, model 123-T-1, 422 watts, is seven inches long; the reaction chamber furnace, model 123-T-2, 584 watts, is eleven inches long. Temperature control for the system is achieved using two chromel-alumel thermocouples installed into the center of each section and connected to two Leeds and Northrup Speedomax H recorder-controllers. The furnaces are connected to the controllers through Struthers-Dunn magnetic circuit breakers.

A series of measurements were made to determine the region of the reaction chamber for which 1200°F. could be maintained. These measurements were obtained by recording the temperature through the entire heated zone while maintaining a constant temperature of 1200°F. at the center. The determination is shown graphically in Figure B-1. It is evident from these measurements that a suitable exposure zone exists for exposing specimens in the three inch center region of the furnace.

Calibration of the temperature control in the zone was done using a calibrated chromel-alumel thermocouple and potentiometer. This thermocouple had previously been calibrated against a platinum-platinum/rhodium (10 per cent)

Figure B-1. Temperature Distribution Through Reaction Chamber.

couple calibrated by the National Bureau of Standards. The platinum-platinum/rhodium couple was accurate to within $\pm$ 1°C. The calibrated thermocouple was inserted into the reaction chamber next to the experimental couple which was connected to a Leeds and Northrup recorder. Argon was passed through the system at a rate of 0.3 cubic foot per hour, and the system was heated to intermittent temperatures in the range 800°F. to 1500°F. The system was allowed to equilibrate for one-half hour at which time simultaneous readings of both couples were recorded. For the entire temperature range, the average deviation of the experimental recorder was $\pm$ 11°F. from the value obtained using the calibrated couple. The greatest deviation occurred at a recorded temperature of 1450°F. which was 14°F. higher than the calibrated value. The Leeds and Northrup Speedomax H is rated by the manufacturer as accurate to within $\pm$ 15°F. Although the calibration indicated that the control accuracy for the unit was better than that given by the manufacturer, the measurements had not been made for prolonged periods of time. Therefore, it was considered best to rate the control as accurate to within $\pm$ 15°F., in accordance with the instrument's rating.

Exhaust gases are passed from the exposure zone through

an oil bath. The bath is a three liter beaker filled with oil into which an inverted funnel is placed. The gas is bubbled through the oil, collected by the funnel, and conducted to the atmosphere outside the building by a copper tube. The purpose of the bath is to prevent air from entering the system from an open exhaust port. Also included in the exhaust duct is a flow meter to measure the gas flow rate. It was desired to keep the carbon monoxide rate through the system as small as possible so that the velocity of the gas would not create an erosive effect and carry reaction products from the specimen's surface into the gas stream. The minimum flow rate which could be controlled was used. This value was determined to be 0.3 cubic foot per hour $\pm$ 0.1 cubic foot per hour.

Several accessories were added to the system to obtain experimental data on electrical resistance changes of Type 316 stainless steel during exposure and on gas composition after reaction. A Rubicon Standard Kelvin Bridge, Catalog Number 1600, was connected to the system as shown in Figure B-2 to measure resistances during reaction. The bridge is capable of measuring resistances as large as 1.0 ohm to an accuracy of 0.0001 ohm. It was desired to use approximately 20 inch lengths of 0.010 inch

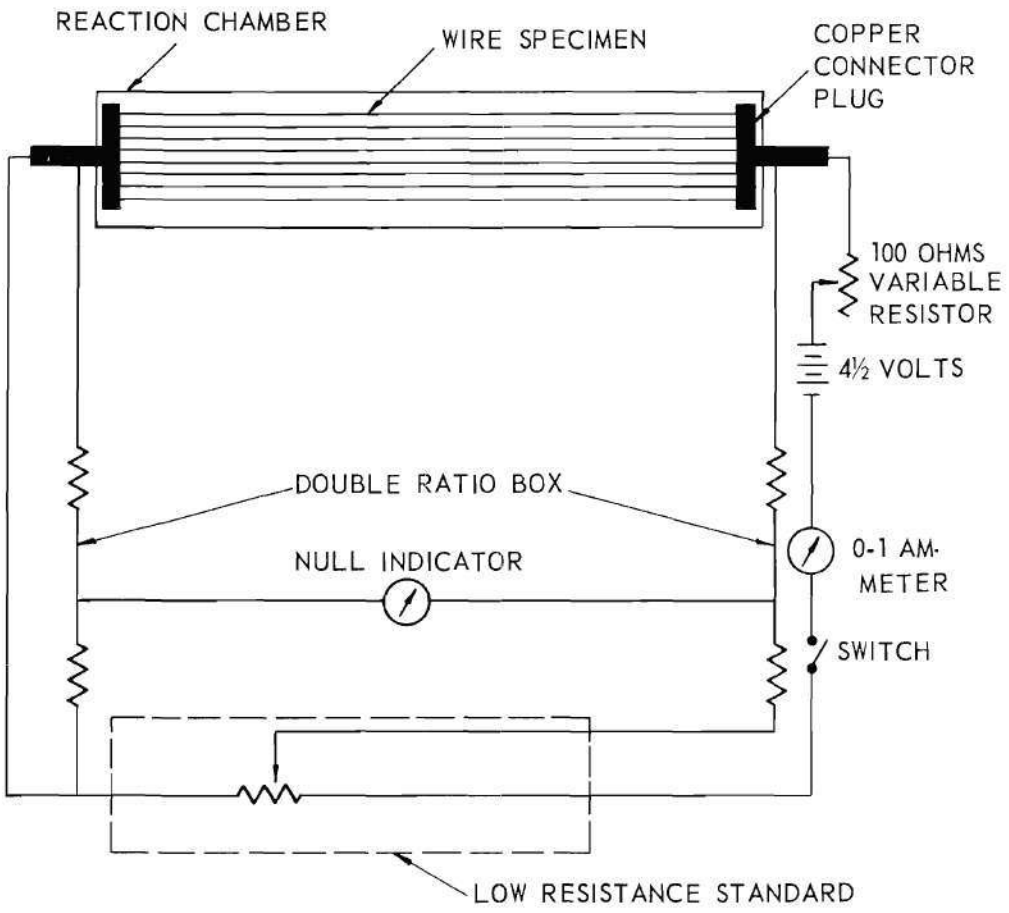


Figure B-2. Kelvin Bridge Apparatus for Measuring Resistance Changes of Type 316 Stainless Steel Wire.

diameter Type 316 stainless steel wire. The resistivity of Type 316 stainless steel is 74 x 10^{-6} ohm centimeters; thus, a wire of these dimensions would have a resistance of about 9 ohms. Therefore, it was necessary to run several wires connected or parallel so that the total resistance would be less than 1.0 ohm. This was accomplished by soldering from 12 to 25 wires to copper plugs which were installed at either end of the reaction tube. The connections from the bridge were soldered to these plugs as shown in the diagram. The change in electrical resistance of Type 316 stainless steel with temperature was determined so that an estimate of the error in recorded measurements due to temperature fluctuations could be calculated. This determination was made by measuring the resistance of 12 stainless steel wires connected in parallel at intermittent temperatures in the range 900°F. to 1400°F. Argon was circulated through the system to prevent oxidation. The values obtained were converted to resistances of a single wire and plotted versus temperature. This is shown in Figure B-3. The value of $\frac{\Delta R}{\Delta T}$ was obtained from this figure and is 9.5 x 10^{-4} ohm per °F.

To analyze the composition of experimental gas after reaction with Type 316 stainless steel, a cold trap was connected just outside the reaction chamber to quench the exit

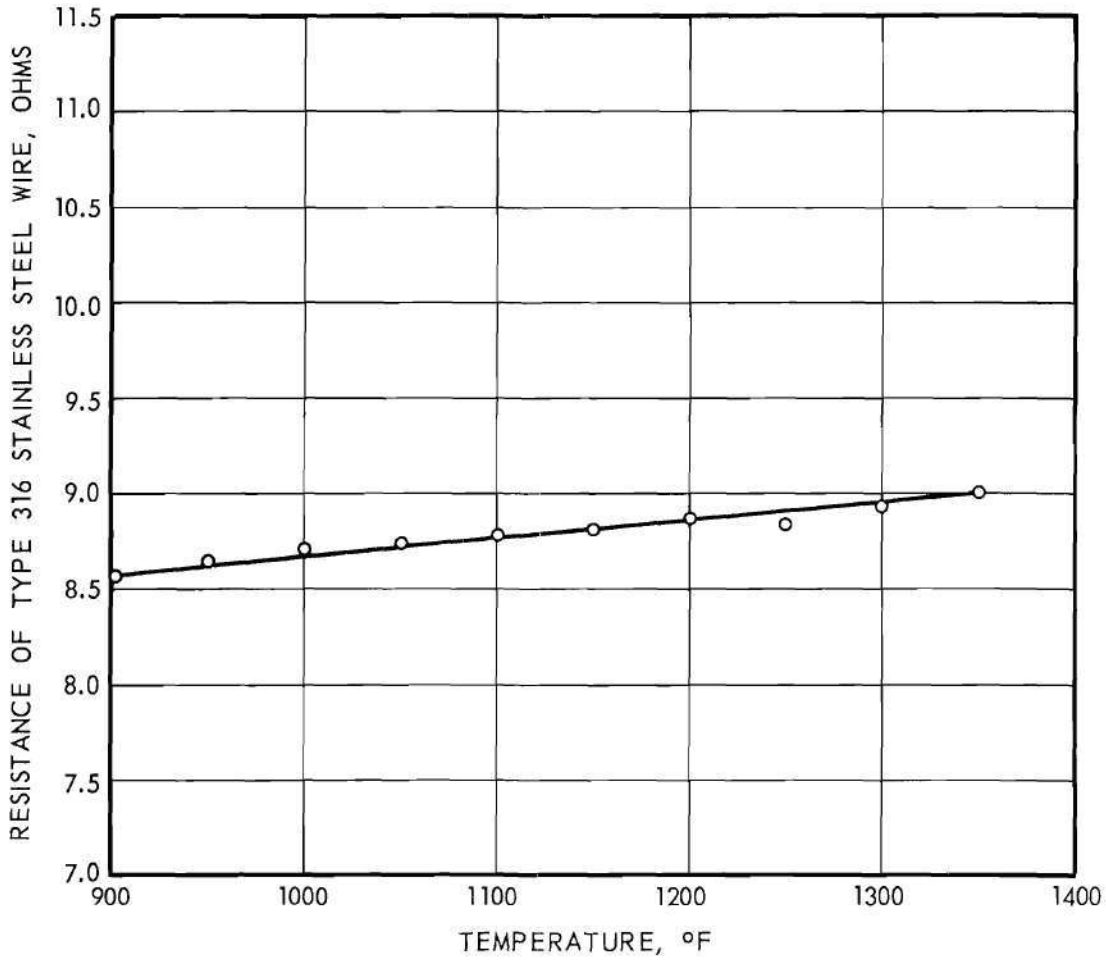


Figure B-3. Electrical Resistance of Type 316 Stainless Steel Wire in Argon Atmosphere.

gases. The trap is an eight inch, 200 milliliter cell contained in a Dewar flask filled with liquid nitrogen. The flask and trap are removable from the system so that the contents can be maintained at liquid nitrogen temperature (-192°C.) while transferring to an infrared spectometer.

Experimental Procedure

The experimental procedure established for exposing specimens to carbon monoxide can be divided into two routines, one for exposing stainless steel wires, and one for exposing transmission specimens of iron, nickel, and stainless steel. The procedure for stainless steel wire specimens is as follows:

1. Wind up approximately five grams of Type 316 stainless steel wire into small, loosely packed bundle.
2. Clean ultrasonically for several minutes in xylene.
3. Dry, weigh, record weight.
4. Insert sample into exposure zone.
5. Turn on carbon monoxide, allow flow to continue several minutes to purge air from entrance line.
6. Turn on argon, allow to purge system for one-half hour.
7. Turn on recorder-controllers and set controllers at reaction temperature.

8. Check system for leaks.

9. Introduce carbon monoxide after system has been at reaction temperature one-third hour.

10. Check flow rate.

11. After sample exposure is complete, stop flow of carbon monoxide, introduce argon.

12. Turn off furnaces, remove quartz tube from the furnace region.

13. Allow specimens to cool to room temperature in argon.

14. Remove specimens from chamber.

15. Shut off recorders, seal off carbon monoxide and argon.

16. Reweigh specimens, record weight.

17. Remove deposits from surface ultrasonically, reweigh. Continue process until a constant weight is obtained. Record.

18. Place sample in dessicator.

19. Filter solution, collect deposits. Dry, store in dessicator.

The procedure followed for exposure of transmission specimens is identical to the procedure given above, except that steps 1-3 and 16-19 are omitted.

APPENDIX C
EXPERIMENTAL RESULTS ON IRON

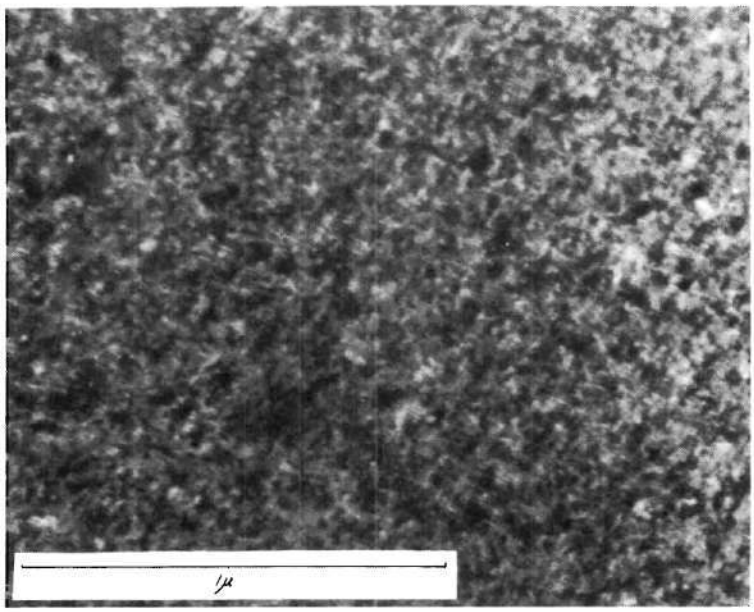


Plate 1. Iron Prepared by Vapor Deposition

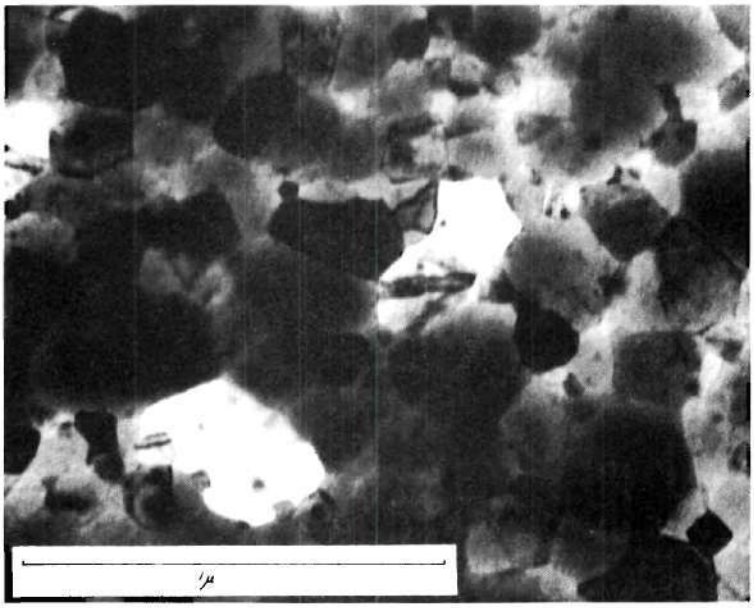


Plate 2. Iron Exposed to Carbon Monoxide for 5 Minutes at 1200°F. Note Particle Development in Deposits and Attack in Grain Boundaries.

Figure C-1. Experimental Observations on Iron-Carbon Monoxide Reaction at 1200°F.

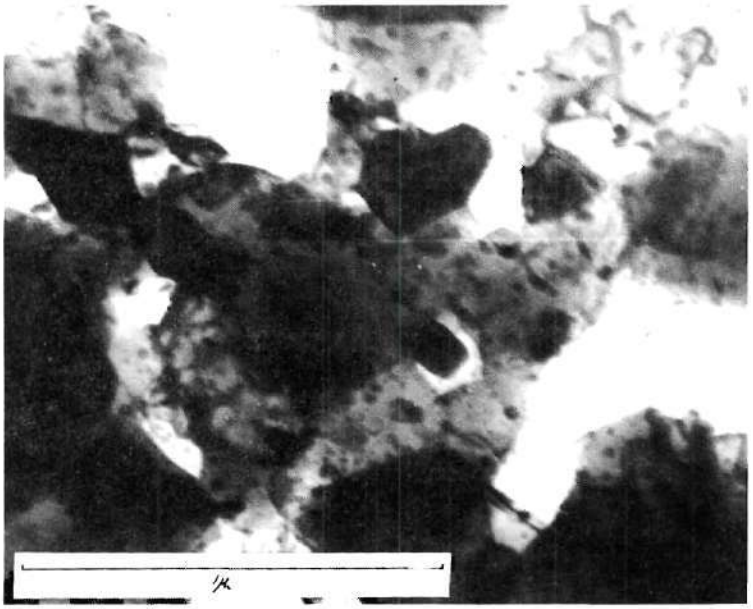


Plate 3. Iron Exposed to Carbon Monoxide for 10 Minutes at 1200°F.

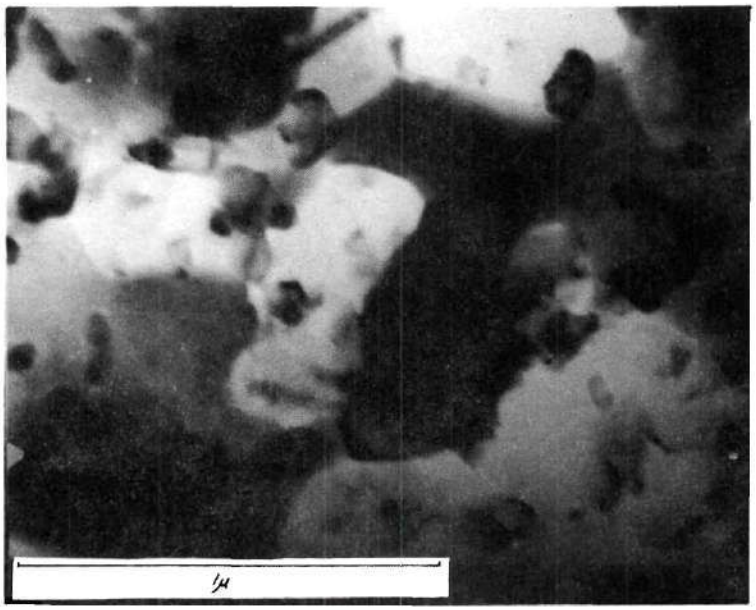


Plate 4. Iron Exposed to Carbon Monoxide for 15 Minutes at 1200°F.

Figure C-1 (Continued). Experimental Observations on Iron-Carbon Monoxide Reaction at 1200°F.

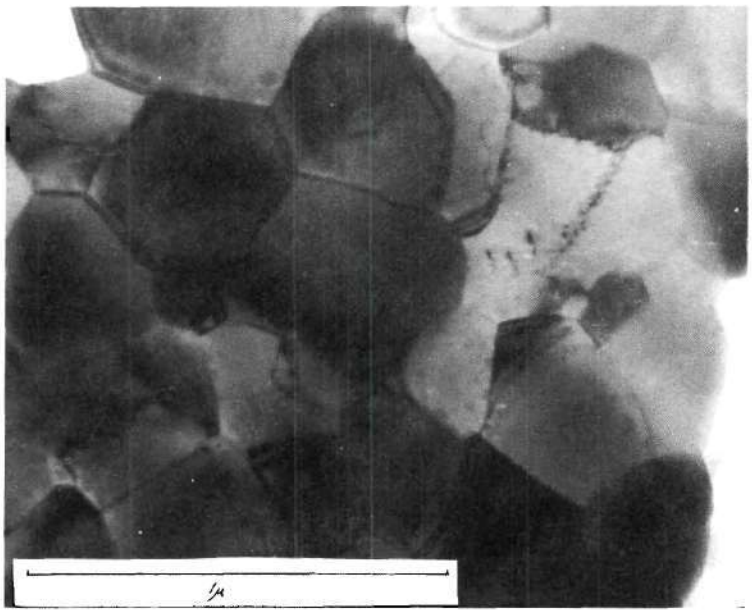


Plate 5. Iron Exposed to Air for One Minute and Carbon Monoxide for 5 Minutes at 1200°F.

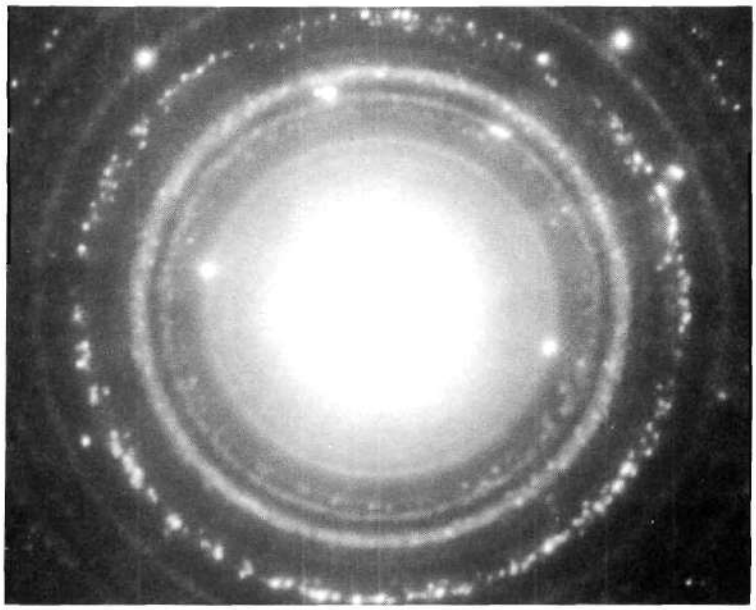


Plate 6. Selected Area Diffraction Pattern from Iron Specimen Exposed to Carbon Monoxide at 1200°F for 5 Minutes.

Figure C-1 (Continued). Experimental Observations on Iron-Carbon Monoxide Reaction at 1200°F.

APPENDIX C

Table C-1

Experimental Results of Selected Area Diffraction of Iron Exposed to Carbon Monoxide

Sample 1a		Sample 1b	
Exposure Time:	15 minutes	Exposure Time:	15 minutes
Temperature:	1200°F	Temperature:	1200°F
Carbon Monoxide Flow Rate:	0.3 foot^3/hour	Carbon Monoxide Flow Rate:	0.3 foot^3/hour

d, Å	I/I_o	d, Å	I/I_o
2.87	m	2.85	m
2.65	m	2.60	w
2.50	s		
2.40	w		
2.16	s	2.10	vs
2.00	vs	2.05	vs
1.90	w	1.94	w
1.82	w	1.85	w
		1.80	m
1.70	m	1.72	m
1.62	w	1.55	m
1.39	m	1.37	w
1.24	m	1.24	w
1.11	m		

m = medium
s = strong
v = very
w = weak

APPENDIX C

Table C-1

(Continued)

Sample 2a		Sample 2b	
Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour	
d, Å	I/I_o	d, Å	I/I_o
2.76	w	2.79	w
2.64	m	2.65	m
2.57	w	2.57	w
2.50	m	2.50	m
2.40	vs	2.40	vs
2.30	vw	2.29	vw
2.14	vs	2.14	vs
2.03	s	2.04	s
1.82	m	1.82	m
1.70	m	1.70	m
1.60	m	1.59	m
1.51	vw	1.52	vw
1.42	vw	1.42	vw
1.40	vw	1.38	vw
1.22	s	1.20	s
		1.04	vw

APPENDIX D
EXPERIMENTAL RESULTS ON NICKEL

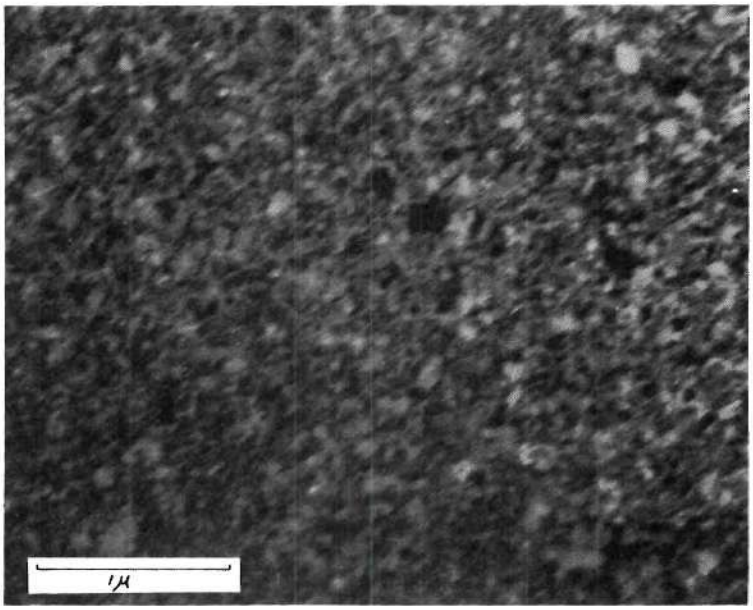


Plate 1. Nickel Prepared by Vapor Deposition.

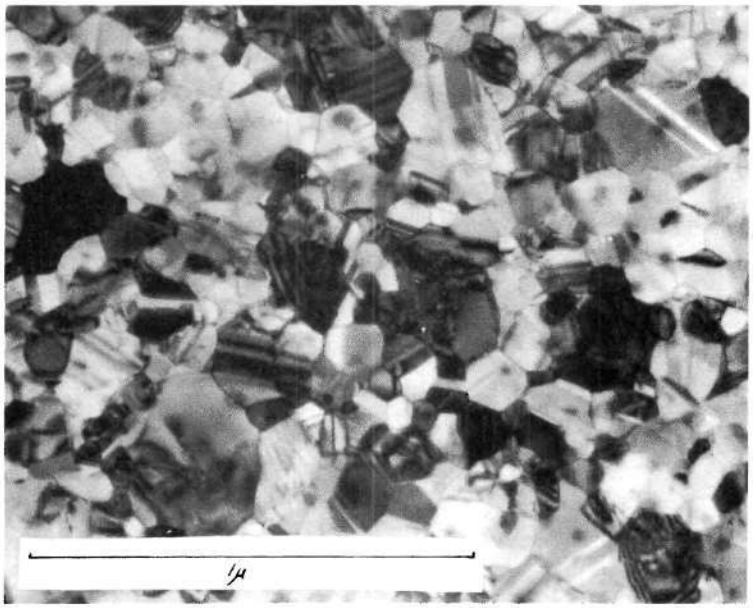


Plate 2. Exposed to Carbon Monoxide at 1200°F for One Minute.

Figure D-1. Experimental Observations on Nickel-Carbon Monoxide Reaction at 1200°F.

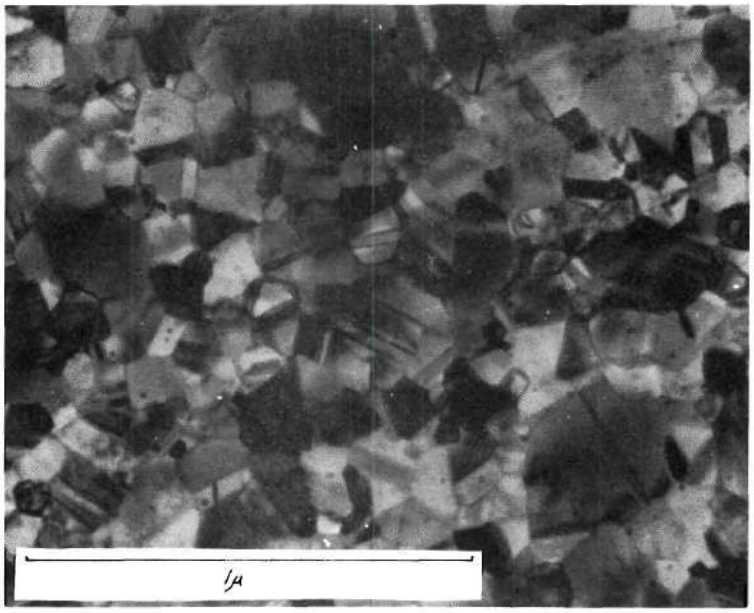


Plate 3. Nickel Exposed to Carbon Monoxide at 1200°F for 5 Minutes.

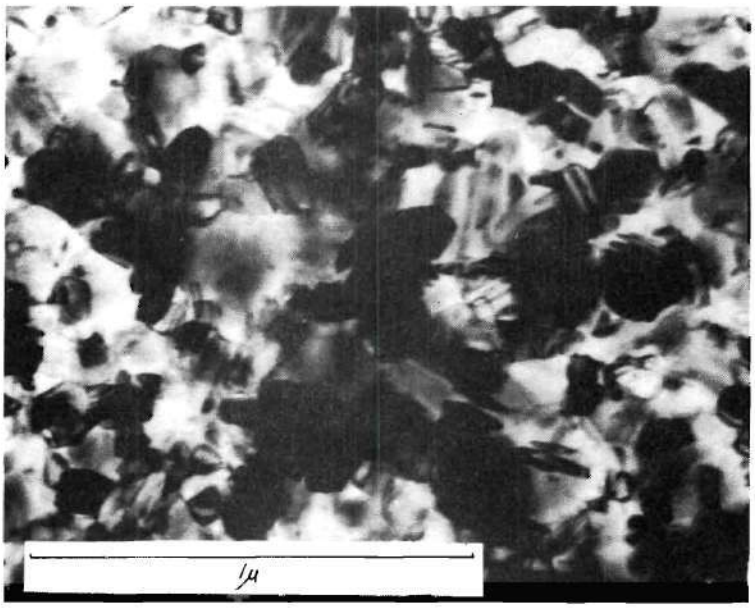


Plate 4. Nickel Exposed to Carbon Monoxide at 1200°F for 45 Minutes.

Figure D-1 (Continued). Experimental Observations on Nickel-Carbon Monoxide Reaction at 1200°F.

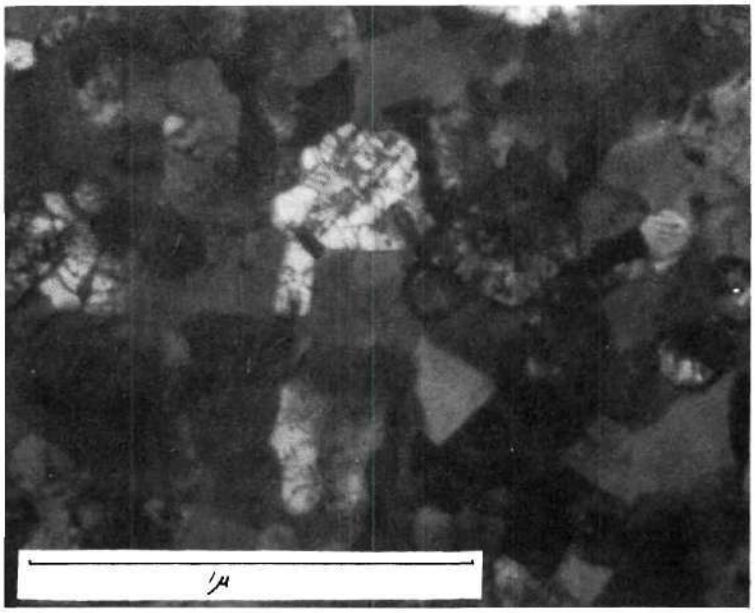


Plate 5. Nickel Exposed to Air at 1200°F for One Minute and to Carbon Monoxide at 1200°F for 15 Minutes.

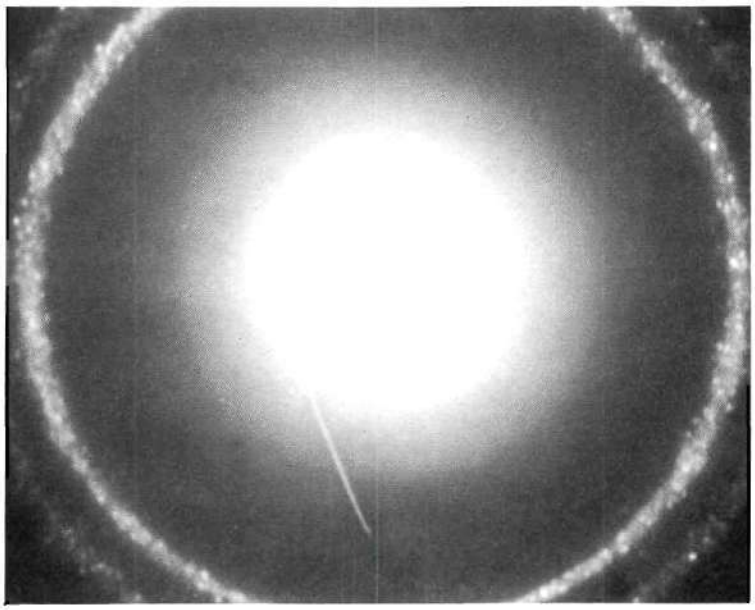


Plate 6. Selected Area Diffraction Pattern from Nickel Exposed to Carbon Monoxide at 1200°F for 15 Minutes.

Figure D-1 (Continued). Experimental Observations on Nickel-Carbon Monoxide Reaction at 1200°F.

APPENDIX D

Table D-1

Experimental Results of Selected Area Diffraction of Nickel Exposed to Carbon Monoxide

Sample 1		Sample 2		Sample 3	
Exposure Time: 1 minute Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 2 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour	
d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o
2.04	vs	2.04	vs	2.04	vs
1.76	s	1.76	s	1.76	s
1.24	w	1.24	w	1.24	w

APPENDIX D

Table D-2

Experimental Results of Selected Area Diffraction of Nickel Exposed to Oxygen and Carbon Monoxide

Sample 1a		Sample 1b		Sample 2	
Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 15 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour	
d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o
2.39	s	2.40	vs		
2.06	vs	2.06	vs	2.10	vs
1.75	m			1.80	s
1.47	m	1.47	m		
1.25	w	1.25	w	1.24	m
1.20	w	1.20	w		
				0.95	m

APPENDIX E
EXPERIMENTAL RESULTS ON AISI TYPE 316 STAINLESS STEEL

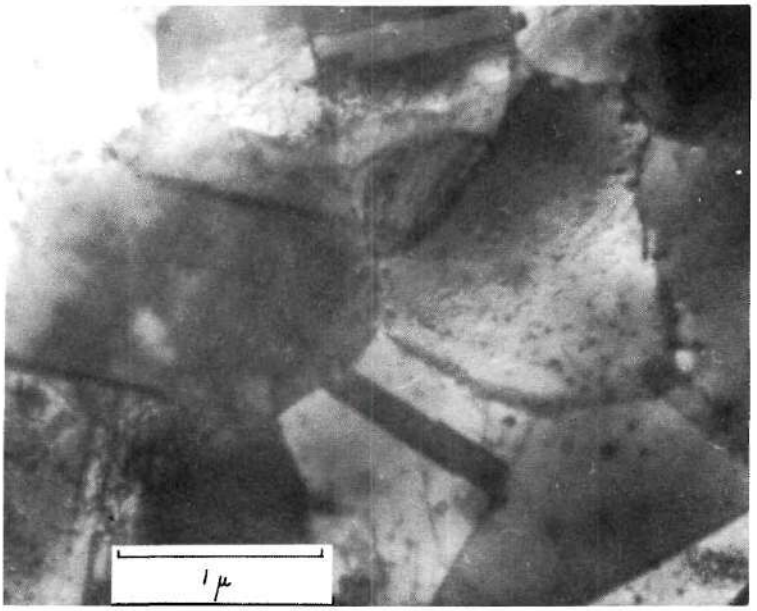


Plate 1. Type 316 Stainless Steel Prepared by Electropolishing.

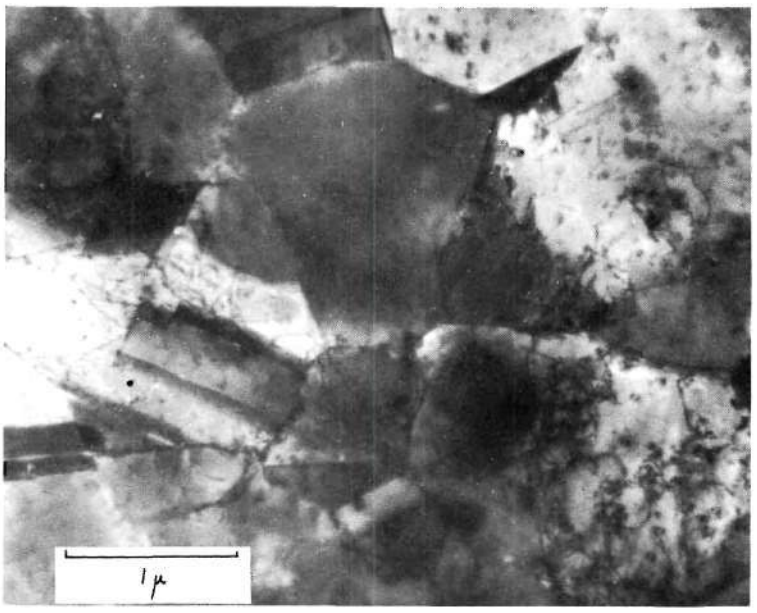


Plate 2. Type 316 Stainless Steel Exposed to Carbon Monoxide at 1200°F for 5 Minutes. Carbon Monoxide Pressure = 50 Microns of Mercury.

Figure E-1. Experimental Observations on Type 316 Stainless Steel-Carbon Monoxide Reaction at 1200°F.

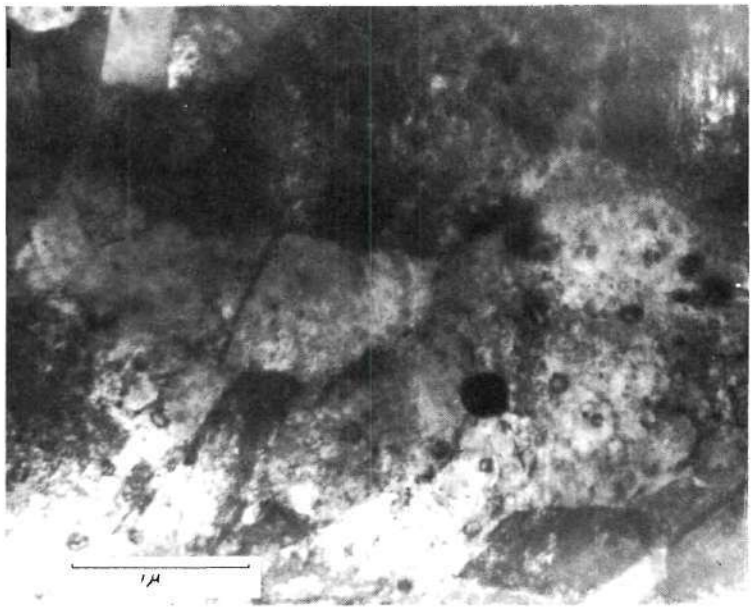


Plate 3. Type 316 Stainless Steel Exposed to Carbon Monoxide at 1200°F for 5 Minutes. Carbon Monoxide Pressure = 50 Microns of Mercury.

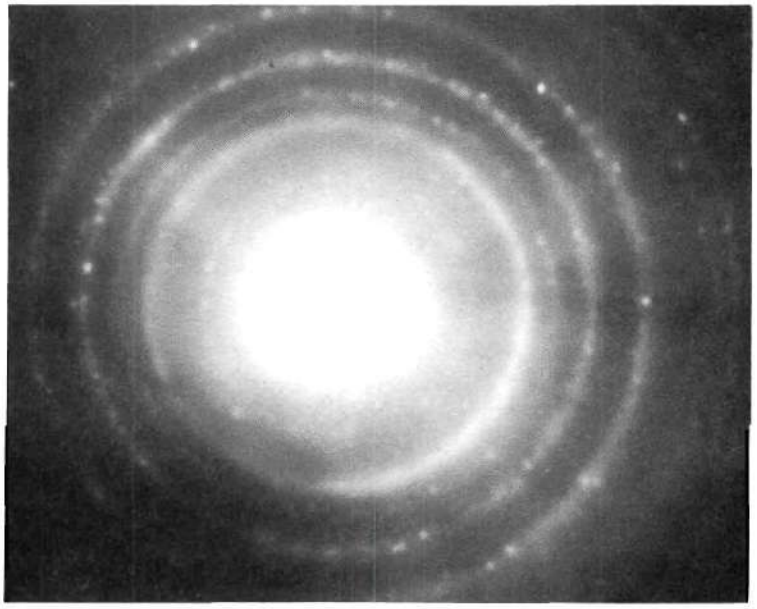


Plate 4. Selected Area Diffraction Pattern for Type 316 Stainless Steel Exposed to Carbon Monoxide at 1200°F for 10 Minutes.

Figure E-1 (Continued). Experimental Observations on Type 316 Stainless Steel-Carbon Monoxide Reaction at 1200°F.

Plate 5. Run 12-D Carbonaceous Deposits on Type 316 Stainless Steel Wire After Exposure to Carbon Monoxide at 1200°F for 72 Hours. Note Filament Type Growth. (x75)

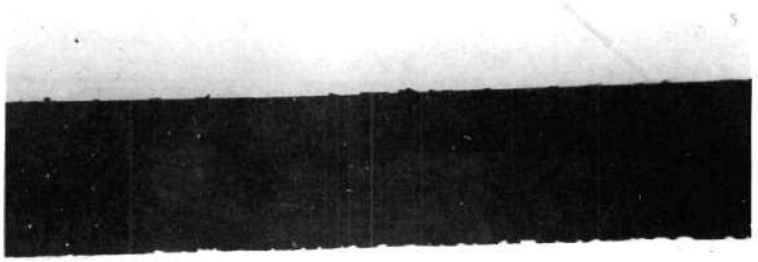


Plate 6. Same as Plate 5 Showing Ultrasonically Cleaned Surface. (x75)

Figure E-1 (Continued). Experimental Observations on Type 316 Stainless Steel-Carbon Monoxide Reaction at 1200°F.

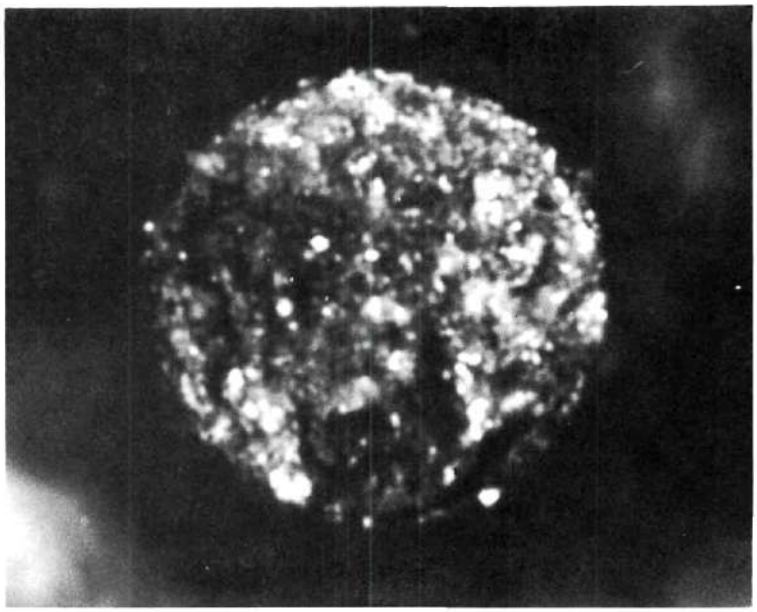


Plate 7. Same as Plate 5 Showing Intergranular Fracture. (x250)

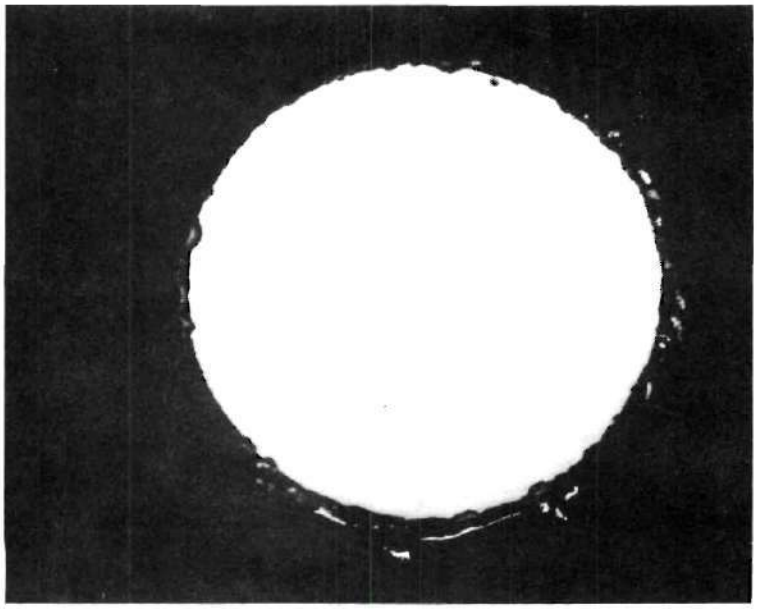


Plate 8. Same as Plate 5 Polished to Show Surface Attack. Metal in Removed Regions is Due to Burring. (x250)

Figure E-1 (Continued). Experimental Observations on Type 316 Stainless Steel-Carbon Monoxide Reaction at 1200°F.

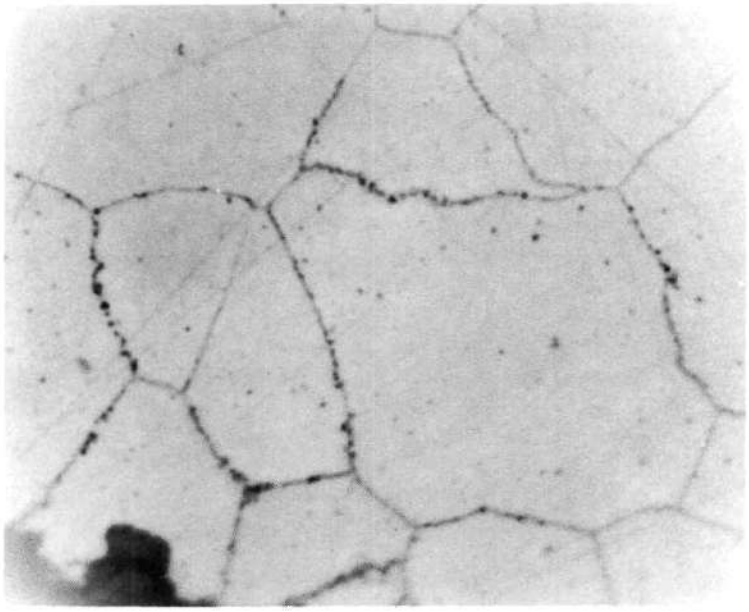


Plate 9. Same as Plate 5 Showing Metal Removal and Carbide Precipitation. 10% Oxalic Acid Etch, 1½ Volts, One Second. (x1000)

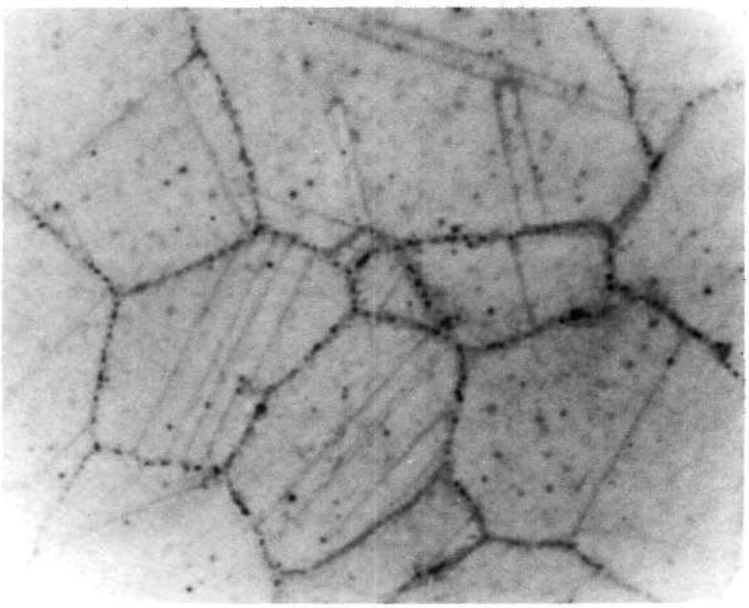


Plate 10. Same as Plate 5 Showing Carbide Precipitation at Center of Wire. 10% Oxalic Acid Etch, 1½ Volts, One Second. (x1000)

Figure E-1 (Continued). Experimental Observations on Type 316 Stainless Steel-Carbon Monoxide Reaction at 1200°F.

APPENDIX E

Table E-1

Experimental Results of Selected Area Diffraction of Type 316 Stainless Steel Exposed to Carbon Moncxide

Sample 1		Sample 2		Sample 3		Sample 4		Sample 5	
Exposure Time: 1 minute Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 1 minute Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 2 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 2 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour	
d,Å	I/I_o	d,Å	I/I_o	d,Å	I/I_o	d,Å	I/I_o	d,Å	I/I_o
				2.84	m	2.84	w		
						2.71	vw	2.75	vw
2.58	m	2.60	s	2.65	w	2.56	vw	2.61	w
2.50	w	2.50	m	2.56	m	2.50	s	2.50	m
2.35	s	2.36	s	2.32	s	2.35	m	2.40	vs
2.20	w	2.21	m					2.24	m
				2.04	m			2.02	w
				1.99	vs			1.95	m
		1.89	m					1.85	m
				1.67	w			1.67	w
				1.37	vw	1.44	m		
				1.18	vw				
				1.13	vw				

APPENDIX E

Table E-1

(Continued)

Sample 6		Sample 7		Sample 8		Sample 9		Sample 10	
Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 5 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 10 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour		Exposure Time: 10 minutes Temperature: 1200°F Carbon Monoxide Flow Rate: 0.3 foot^3/hour	
d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o	d, Å	I/I_o
		2.79	w	2.75	w	2.75	w	2.75	w
2.60	m	2.60	w			2.65	w		
2.50	m	2.52	m	2.50	m	2.52	m	2.54	s
2.40	vs	2.40	vs	2.40	vs	2.40	vs	2.40	m
2.35	s			2.35	m			2.34	vs
		2.25	m			2.23	m		
2.09	w	2.09	w	2.11	w	2.10	m	2.14	vs
2.02	vw			2.07	w			2.06	m
1.95	w	1.96	w	1.95	w				
1.85	m	1.85	m	1.84	m	1.79	w	1.84	m
1.67	w			1.71	w	1.70	m	1.70	m
				1.50	w				
1.40	w								
1.21	vw			1.21	vw				
1.16	vw			1.17	vw			1.15	w
1.09	w								

APPENDIX E

Table E-2

Experimental Results of Weight Changes of Type 316 Stainless Steel After Exposure to Carbon Monoxide at 1200°F

			Specimen Conditions After Exposure[a]					
			Before Ultrasonic Cleaning			After Ultrasonic Cleaning		
Run Number	Time	Initial Weight W_o	Total Weight W_1	Weight Change	Percent Weight Change	Final Weight W_2	Weight Change	Percent Weight Change
	Hours	Grams	Grams	Grams		Grams	Grams	
4B	5	5.5737	--	--	--	5.6950	0.1213	1.605
5B	24	4.4487	--	--	--	4.4479	-0.0009	-0.02
7B	1	5.7322	5.7425	0.0103	0.18	5.7407	0.0085	0.15
8B	2	4.5340	4.9421	0.0081	0.16	4.9382	0.0042	0.09
9B	5	5.2741	5.3446	0.0705	1.34	5.3018	0.0277	0.50
13B	17	5.7190	5.9498	0.2308	4.04	5.7461	0.0271	0.47
14B	29	5.2626	5.5500	0.2824	5.36	5.3035	0.0409	0.78
15B	20	4.7100	4.8737	0.1637	3.47	4.7629	0.0529	1.07
16B	2	5.2127	5.2254	0.0117	0.25	5.2199	0.0072	0.14
17B	15	6.7150	6.8664	0.1949	2.92	6.7655	0.0940	1.41
18B	24	6.5424	6.7914	0.2490	3.82	6.5908	0.0484	0.74
19B	10	5.3863	5.5158	0.1295	2.41	5.4347	0.0484	0.90
23B	35	5.1963	5.4299	0.2336	4.49	5.1802	-0.0161	-0.31
31B	1	3.5299	3.5366	0.0067	0.19	--	--	--
32B	3	5.3747	5.3993	0.0246	0.48	--	--	--

[a]Carbon monoxide flow rates approximately 0.3 cubic foot/hour

APPENDIX E

Table E-3

Experimental Results of X-ray Diffraction Analyses

Radiation: CuKα (50Kv, 40ma)
Filter: Nickel
Sample: Carbonaceous Deposits from Type 316 Stainless Steel Samples Exposed to Carbon Monoxide at 1200°F

Specimen 1 Scan Speed: 2°(2θ)/minute		Specimen 2 Scan Speed: ½°(2θ)/minute	
d	I/I_o	d	I/I_o
3.37	100	3.37	100
2.71	8	2.71	6
2.50	13	2.50	9
2.06	75	2.06	75
		1.93	3
1.79	20	1.79	28
1.77	13	1.77	15
1.69	12	1.69	15
1.28	18	1.27	12
1.24	2	1.24	6
1.08	10	1.08	8

APPENDIX E

Table E-4

Experimental Results of Electrical Resistance Changes of Type 316 Stainless Steel During Exposure to Carbon Monoxide

Operating Conditions:
Temperature: 1200°F
Carbon Monoxide flow rates approximately 0.3 cubic foot/hour

Run Number:	11D		12D		25D	
	12 Wires		25 Wires		21 Wires	
Time of Exposure	Total Resistance	Resistance of Single Wire	Total Resistance	Resistance of Single Wire	Total Resistance	Resistance of Single Wire
	ohm	ohms	ohm	ohms	ohm	ohms
0.0	0.75408	9.05	0.37151	9.30	0.39805	8.36
0.1	0.75408	9.05	0.37150	9.30	0.39808	8.36
0.2	0.75491	9.06	0.37158	9.30	--	--
0.3	0.75513	9.06	0.37222	9.30	--	--
0.5	0.75885	9.10	0.37265	9.32	0.39871	8.38
0.8	0.76200	9.14	0.37306	9.33	--	--
1.0	0.76277	9.16	0.37311	9.33	0.39944	8.38
1.5	--	--	0.37655	9.40	0.40611	8.53
2.0	0.80925	9.70	0.37995	9.45	0.41005	8.60
2.2	0.81235	9.75	--	--	--	--
2.5	--	--	--	--	0.41637	8.74
3.0	0.79515	9.55	0.37724	9.42	0.41632	8.74
3.5	--	--	--	--	0.41374	8.69
4.0	--	--	--	--	0.41038	8.60
4.5	--	--	--	--	0.40850	8.57
5.1	--	--	--	--	0.40665	8.53
5.5	0.75435	9.05	0.36505	9.13	0.40219	8.43
6.0	0.75290	9.04	--	--	0.39875	8.36
6.5	0.75254	9.04	--	--	0.39411	8.27
7.0	0.75283	9.04	--	--	0.39411	8.27
8.0	0.75351	9.04	--	--	0.39475	8.28
8.5	--	--	--	--	0.39491	8.29
9.0	--	--	--	--	0.39467	8.28
9.5	--	--	--	--	0.39470	8.28
10.0	--	--	--	--	0.39479	8.28
18.5	0.76815	9.22	0.37500	9.37	--	--
19.0	0.76813	9.22	--	--	--	--
20.0	--	--	0.37615	9.40	--	--
23.0	--	--	0.37035	9.25	--	--
24.5	--	--	0.36955	9.24	--	--
48.0	--	--	0.37325	9.33	--	--
72.0	--	--	0.37405	9.35	--	--

APPENDIX E

Table E-5

Rate of Change of Electrical Resistance of Type 316 Stainless Steel with Time during Carbon Monoxide Exposure at 1200°F

Time of Exposure	Rate of Change = $\frac{\Delta R}{\Delta T}$ $\frac{\text{ohms}}{\text{hour}}$		
Hours	Run 11D	Run 12D	Run 25D
0.5	0.18	0.05	--
1.0	0.15	0.10	0.32
1.5	0.59	0.15[a]	0.20
2.0	1.00[a]	0.07	0.29
2.3	--	--	0.48[a]
2.5	-0.14	-0.14	0.08
3.0	-0.32[b]	-0.20[b]	-0.05
3.5	-0.31	-0.18	-0.14
4.0	-0.25	-0.08	-0.14
4.5	-0.18	-0.05	-0.14
5.0	-0.10	-0.04	-0.15
5.5	-0.04	-0.05	-0.16[b]
6.0	0.00	--	-0.14
6.5	0.00	--	-0.08

[a]Maximum rate of change during run

[b]Minimum rate of change during run

APPENDIX E

Table E-6

Experimental Results of Infrared Analyses of Quenched Exit Gases

Operating Conditions:

Prism:	NaCl
Resolution:	927
Response:	11
Gain:	5
Scan Time:	32
Suppression:	8
Expansion:	1X

Carbon Monoxide Standard			Gaseous Reaction Products[a] Sample 4-Bg			Sample 17-Bg		
μ	cm^{-1}	% abs.	μ	cm^{-1}	% abs.	μ	cm^{-1}	% abs.
			1.95	5140	4			
2.26	4340	5	2.24-2.36	4460-4240	1	2.38	4200	6
			2.64	3790	55	2.66	3760	70
			2.72	3680	49	2.75	3640	64
			3.30	3040	9			
			3.44	2910	9	3.44	2910	18
			4.26	2350	100	4.40	2275	100
4.55	2200	100	4.56	2195	46	4.58	2190	97
4.67	2140	90	4.64	2160	42	4.70	2125	92
						8.37	1195	22
						8.45	1184	25
			8.70	1150	23	8.95	1118	10
						9.05	1105	10

[a]Collected in 15 minute quench periods

BIBLIOGRAPHY

Literature Cited

1. Walter Baukloh, "The Destructive Effects of Gases Containing Carbon Monoxide and Carbon Dioxide," Die Chemische Fabrick 13, No. 6, (1940), 101-104.

2. A. Juliard, R. Rayet, and A. Ludé, "A Kinetic Study of the Dissociation of Carbon Monoxide Accompanying the Reduction of Metallic Oxides," Discussions Faraday Society, No. 4, translated by J. H. E. Jeffes, (1948), 193-196.

3. W. R. Davis, R. J. Slawson, and G. R. Rigby, "An Unusual Form of Carbon," Nature 171, (1953), 756.

4. W. B. Hoyt and R. H. Caughey, "High Temperature Metal Deterioration in Atmospheres Containing Carbon Monoxide and Hydrogen," Corrosion 15, (1959), 627t-630t.

5. Ya. B. Kagan, A. N. Bashkirov, E. V. Kamzolkina, and A. Ya. Rozovsky, "The Kinetics of Conversion of Carbon Monoxide in the Presence of Iron Catalysts," Zhurnal Fizicheskoi Khimii 33, pt. 2, (1959), 2706-2711.

6. Seagraves, William Benjamin, Corrosion of Nickel Containing Materials by Carbon Monoxide at Elevated Temperatures Ph.D. Thesis, Georgia Institute of Technology, 1960.

7. X-ray Pattern Powder Data File, American Society for Testing Materials, Philadelphia, Pennsylvania, Special Technical Publication, 48J.

8. L. J. E. Hofer, E. Sterling, and J. T. McCartney, "Structure of the Carbon Deposited from Carbon Monoxide on Iron, Cobalt and Nickel," Technical Report Number 1131-228, Synthetic Fuels Research Branch, Fuels Technology Division, United States Bureau of Mines, Region VIII, (1954).

9. Elliott, John F. and Glisser, Molly, Thermochemistry for Steelmaking, Reading, Massachusetts: Addison-Wesley Publishing Company, Inc., (1960).

10. H. D. Rix, "The Infrared and Raman Spectra of Carbon Suboxide," Journal Chemical Physics 22, (1954), 429-433.

11. Phillip J. Launer, "Tracking Down Spurious Bonds in Infrared Analysis," Perkin-Elmer Corporation News Publication, (1962).

12. Edgar C. Bain, "Trends in Metallurgical Research in the United States," Journal Iron and Steel Institute 180, (1955), 193-212.

13. J. Washburn, A. Kelly, and G. K. Williamson, "Direct Observation of Dislocations in Magnesium Oxide," Philosphical Magazine 5, (1960), 192-193.

14. Thomas, Gareth, Transmission Electron Microscopy of Metals, New York: John Wiley and Sons, Inc., (1962).

Other References

1. P. Bastien and M. Colombie, "Oxydation du fer et des aciers par l'anhydride carboniques a chaud et sous pression," Memoires Scientifiques Rev. Metallurg., LIX, No. 6, (1962), 454-460.

2. W. Baukloh, "Destruction of Cast Iron at Elevated Temperatures by Gases Containing Carbon Monoxide," Metallwissenschaft 18, No. 3, (1939), 57-59.

3. K. Chatterjee, and P. P. Das, "Nature of the Catalyst in the Decomposition of Carbon Monoxide in the Presence of Iron," Nature 173, (1954), 1046.

4. Cullity, B. D., Elements of X-ray Diffraction, Reading, Massachusetts: Addison-Wesley Publishing Company, Inc., (1959).

5. Curtman, Louis J., Introduction to Semimicro Qualitative Chemical Analysis, New York: The MacMillian Company, (1950).

6. R. Eberle and R. D. Wylie, "Attack on Metals by Synthesis Gas from Methane-Oxygen Combustion," Corrosion 15, (1959), 622t-626t.

7. R. M. Fisher and A. Szirmae, "Observations of Dislocations in Thin Foils of Stainless Steel with the Electron Microscope," Engineering Sciences VII, No. 40, (1960), 103-119.

8. Frost, Arthur A. and Pearson, Ralph G., Kinetics and Mechanism, New York: John Wiley and Sons, Inc., (1953).

9. J. A. Gurklis, L. D. McGraw, and C. L. Faust, "Electropolishing and Chemical Polishing of High-Strength, High-Temperature Metals and Alloys," DMIC Memorandum 98, (1961).

10. Haynie, F. H. and Hochman, R. F., "The Mechanism in the Catalytic Decomposition of Carbon Monoxide," Unpublished Report, (1960).

11. Haynie, F. H. and Hochman, R. F., "Thermocynamic Functions of Iron Pentacarbonyl and Nickel Carbonyl," Unpublished Report, (1960).

12. R. D. Heidenreich, "Electron Microscope and Diffraction Study of Metal Crystal Textures by Means of Thin Sections," Journal of Applied Physics 20, (1949).

13. Handbook of Chemistry and Physics, Hodgmen, Charles D., Editor-in-chief, Chemical Rubber Publishing Company, Cleveland, Ohio, (1956).

14. L. J. E. Hofer, "The Preparation and Properties of Metal Carbides," Report of Investigation Number R. I. 3770, United States Bureau of Mines, (1944).

15. L. J. E. Hofer, E. M. Cohn, and W. C. Peebles, "Isothermal Decomposition of Nickel Carbide," The Journal of Physical and Colloid Chemistry 54, No. 8, (1950), 1161-1169.

16. Holthoff, I. M. and Sandell, E. B., Textbook of Quantitative Inorganic Analysis, New York: The MacMillian Company, (1959).

17. B. E. Hopkinson and H. R. Copson, "Internal Carburization and Oxidation of Nickel-Chromium Alloys in Carbon Monoxide Type Atmospheres," Corrosion 16, (1960), 608t-612t.

18. H. Inouye, "Reactions of Type 304 Stainless Steel with Carbon Monoxide and Carbon Dioxide," Oak Ridge National Laboratories Quarterly Reports, (1960-1961), 82-83, 104-106, 112-113, 126-129.

19. Kehl, George L., Metallographic Laboratory Practice, New York: McGraw Hill Book Company, (1949).

20. F. A. Prange, "Corrosion in a Hydrocarbon Conversion System," Corrosion 15, No. 12, (1959), 619t-621t.

21. Sinnott, Maurice J., The Solid State for Engineers, New York: John Wiley and Sons, Inc., (1953).

22. Smith, Morton C., Alloy Series in Physical Metallurgy, New York: Harper and Brothers, (1956).

23. R. Stickler and A. Vinckier, "Morphology of Grain-Boundary Carbides and its Influence on Intergranular Corrosion of 304 Stainless Steel," Transactions Quarterly 54, Transactions of American Society for Metals, No. 3, (1961).

24. Swalin, Richard A , Thermodynamics of Solids, New York: John Wiley and Sons, Inc., (1962).

25. Weber, Harold C. and Meissnor, Herman P., Thermodynamics for Chemical Engineers, New York: John Wiley and Sons, Inc., (1959).